Investigation of increased UV absorbance, reduced band gap and high quenching luminescence efficiency of quantum dot dispersed nematic mesogen

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Abstract- **The dispersion of $Cd_{1-x}Zn_xS/ZnS$ core/shell QD (x=0.85) in nematic liquid crystal into different concentrations has been examined. The spectroscopic parameters such as UV visible absorbance, photoluminescence (PL) and Fourier transform infrared (FTIR) spectra have been observed for pristine and QD dispersed nematic system. The UV visible absorbance spectra brings to light one absorbance peak corresponding to π-π^* transition. Increased UV absorbance with decreased band gap for dispersed system reveals the strong photo absorption (i.e. quenched luminescence). The remarkable results have been found for 0.1% and 0.25% wt/wt QD dispersed nematic system with an average of 51.7% and 61.7% quenching in PL intensity. The FTIR spectra explain the symmetric and asymmetric C-H stretching vibrations which confirm the quenched PL intensity. The UV visible absorbance, PL and FTIR studies have been performed in order to disclose the nature of QD dispersed nematic system. The upshot of the present study finds its relevance in the field of various display and photonic applications as well as in the photovoltaic devices.**

Key words: **Nematic liquid crystal; Quantum dot; UV visible spectroscopy; Photoluminescence; FTIR**

INTRODUCTION

The unremitting demand for the nanomaterials-liquid crystal composite system and the improvement in the performance of LC based devices has been extensively required by the technological field [1]. The dispersion of nanomaterials into liquid crystals has an influential consequence that removes the obstacles which hampered the performance of display devices. Liquid crystals and its composites have wide range of potential application in opto electronic, photonic and display devices [2-5]. They have immense technological importance in both fundamental and applied aspects [4-7].Quantum dots have been utilized as dopant in liquid crystals due to its size dependent fluorescence and electrical properties [6]. Semiconductors QD are the smart nanomaterials that attracted much attention of consortium of researchers due to their prospective applications in display and electro optical devices [5-8]. These nanomaterials are termed as "smart nanomaterials" due to existence of phenomenon of charge transfer, photo or electro-luminescence and self assembly property therefore they have extensive range of application in fabrication of various electro optic and display devices. Dispersing nematic liquid crystal with semiconductor QDs changes its dielectric and viscoelastic properties which affect the characteristic of dynamic devices based on these systems. Nanoparticles dispersed nematic systems are the promising candidates for controlling the photoluminescence (Pl) intensity in photonic devices [8]. Pl, UV-Visible and band gap evaluations have been performed in order to disclose the nature of QD dispersed nematic system. The quenching in the Pl intensity with increasing concentration and interaction between guest QD and host nematic LC has been analyzed and discussed. The core finding in the investigation reports the quenching in Pl intensity with increased UV absorbance and small band gap for QD dispersed nematic system that find application in photovoltaic, photonic and display devices.

EXPERIMENTAL DETAILS

We have used the positive dielectric anisotropy nematic liquid crystal mixture LC- 2020 which is laterally fluorinated $4^{'}$- alkylphenyl-4-isothiocyanatotolanes and exhibits the phase sequence as Cr $\xleftrightarrow{-20^oC}$ N $\xleftrightarrow{107.7^oC}$ Iso. The synthesis of the nematic mesogen LC-2020 was carried out by our collaborating research group Institute of Chemistry, Warsaw Poland [4, 7]. $Cd_{1-X}Zn_XS/ZnS$ core/shell QD used here for the dispersion, are semiconducting quantum dots with x=0.85 and size 8.5 nm (core diameter 5nm and shell diameter 3.5 nm). The QD dispersed nematic system have been prepared by taking an appropriate amount in the weight ratio (0.1% and 0.25%) of the QDs into pure

nematic and then homogenized with an ultrasonic mixer at 108° C for 1 hour and uniform dispersion of QD was obtained at room temperature 30° C. The LC sample cells used to fill the dispersed system have been fabricated by using highly conducting optically transparent sputtered indium tin oxide (ITO) glass substrates. UV visible absorption study of pristine and QD dispersed system have been carried out using UV visible spectrophotometer (ELICO, SL 210) for a wavelength interval of 250-700 nm at room temperature in spectrum mode. The Tau relation [8] describes the band gap energy which is given by:

$$(\alpha h\nu)^2 = \beta[h\nu - E_g] \text{ ---------------- (1)}$$

Here α is the absorption coefficient, $(h\nu)$ is the photon energy, E_g is the optical band gap, β is the frequency independent constant. The optical band gap has been calculated from intercept of the linear portion of plot on $(h\nu)$ axis. The photoluminescence spectra of pristine and QD dispersed system have been carried out using Cary eclipse fluorescence spectrophotometer (Agilent technologies) in scan mode using 5 nm slit width and 350 nm excitation wavelength. The FTIR study has been performed using Fourier transform infrared spectrophotometer (IR Affinity-1 Shimadzu) in the wavelength range of 400-4000 cm^{-1}. In the experiment background scan and reference scan have been filtered.

RESULTS AND DISCUSSION

Fig.1 illustrates the normalized UV-visible absorbance for pristine LC and QD dispersed nematic system on wavelength scale. The inset of the figure shows the normalized absorbance for core/shell QD. It has been found that UV absorbance increases for QD dispersed system than that of pristine LC. The increment in the magnitude of absorbance is due to charge transfer between the mesogenic molecules and core/shell QD which generates net charge on QD resulting in the permanent dipole moment in them [9]. There is a formation of charge transfer complexes in the doped system due to electronic coupling between the HOMO (highest occupied molecular orbital) of the donor and LUMO (lowest unoccupied molecular orbital) of the acceptor molecule [9]. It is clear from the figure that the centre of absorption peaks was found at 348 nm. It has been attributed to π-π* excitation of π electron system. The low absorption of UV light on either side of absorption peak implies that this region is transparent for UV absorption [9]. The broadness in the peak has been noticed which arises from the absorption of radiation over the band of wavelength (i.e. band spectrum). The origin of band spectrum is probably due to the close packing of the molecules in pristine and QD dispersed nematic system. Since the molecules are closely packed in

the system, therefore they exert influence on each other which disturbs the numerous energy levels and blur the sharp spectral lines into bands.
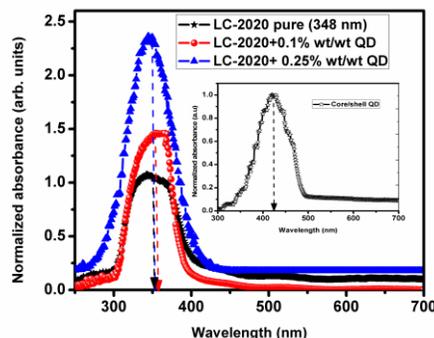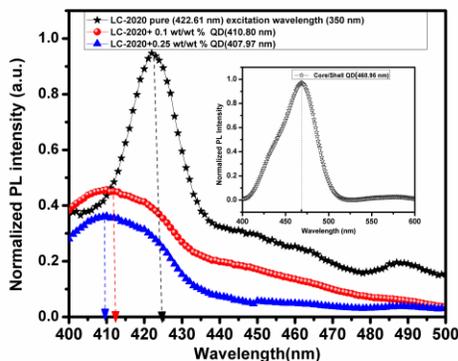

Fig.1. Normalized UV visible spectra of pristine LC and QD dispersed nematic system (0.1% and 0.25% concentration) as a function of wavelength. Inset in the graph represents normalized absorbance spectra for core/shell QD.

Fig.2 shows the plot for $(\alpha h\nu)^2$ and optical band gap. For pristine LC and QD dispersed nematic system the magnitude of optical band gap has been found to be 3.25 eV, 3.20 eV and 3.15 eV respectively. The nature of plot discloses the direct allowed transition. The shape of the transition provides insight into the electron interband transition. The transition region is the absorption edge. The decrement in the band gap for QD dispersed nematic system is explained on the basis of Mott and Davis model [8] according to which shallow states causes band gap to decrease. The increased UV absorbance with decreased band gap implies that the electron transfer from lower state to higher state takes place with strong photo absorption therefore emission should reduce for QD dispersed system (i.e. luminescence quenching). This has also been evident from the PL result discussed in the later part of the paper. Hence our study for UV absorbance and Band gap supports the phenomenon of quenching in PL intensity
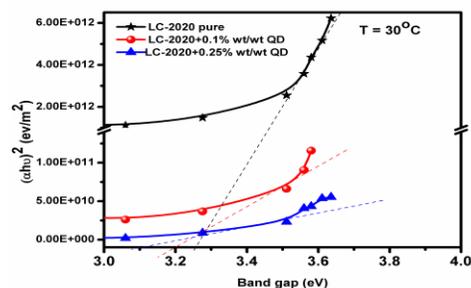
Fig.2. The plot for (αhv)^2 versus band gap for pristine LC and QD dispersed nematic system (0.1% and 0.25% concentration).

Fig.3 shows the normalized PL intensity of pristine and QD dispersed nematic system with variation of concentration. The excitation wavelength for PL is taken to be 350 nm. It is clear from the figure that the maximum PL intensity has been observed at a wavelength of 422.61 nm, 410.80 nm and 407.97 nm respectively for pristine LC, 0.1% and 0.25% QD dispersed system. It has been attributed to blue shift in PL spectra. The PL intensity in both QD dispersed system (0.1% and 0.25%) has been quenched by 51.7% and 62.7% as compared to pristine LC. It can be interpreted that both Core/shell QD (inset) and pristine nematic LC have emission bands which can be combined constructively so that some portion of the PL of pristine LC might be absorbed by QD to give quenched PL intensity for dispersed system . In addition to this the presence of QD significantly modifies the surface topology which leads to change in PL emission [5-6]. PL luminescence quenching suggested that the interaction between LC molecules and core/shell QD leads to non radiative recombination of excitons in photo excited LC molecules. This has also been evident from the FTIR spectra discussed later in this paper. The broadness in the PL peaks is due to the fact that the photons on either side of emission peaks have smaller probability of reabsorption than the photons at the peak center.

Fig.3. Normalized photoluminescence spectra of pristine LC-2020 and QD dispersed nematic system (0.1% wt/wt and 0.25 % wt/wt concentration) as a function of wavelength. Inset in the graph shows the Pl spectra of core/shell QD

Fig.4 shows the FTIR spectra for pristine and QD dispersed system. It is clear from the figure that the normalized transmittance of pristine nematic material has been reduced slightly after the dispersion of QD. This is attributed to absorbance of incident light by the QD. The emergence of peaks or bands at 800-1250 cm^{-1} is intrinsic bands in all thermotropic LCs [5]. 1500-4000 cm^{-1} is the functional group regimes which are the characteristic of specific kind of bonds and used for the identification of

functional groups. There are vibrational bands of C-F bond, C≡ C triple bond and –NCS group (N=C=S) in nematic mesogen. Triple bonds have small intensity and are observed in the range 2200-2250 cm^{-1}, –NCS group are observed in the range of 2050-2100 cm^{-1}. The dominant peaks at 2862 cm^{-1}, 2885 cm^{-1} and 2931 cm^{-1} are due to symmetric & asymmetric C-H stretching vibrations for saturated aliphatic chain. 2400-2800 cm^{-1} regime probably indicates the origin of interaction between core/shell QD and pristine LC-2020. Bands near 3000 cm^{-1} have been appeared due to the interaction between core/shell QD and aromatic core of pristine LC which rearranged C-H vibration. The Pl luminescence quenching is evident from anharmonic molecular vibrations of C-H group of alkyl chain which acts as photo excitation energy acceptor. Therefore this transition is non-radiative electron-vibrational energy transfer.
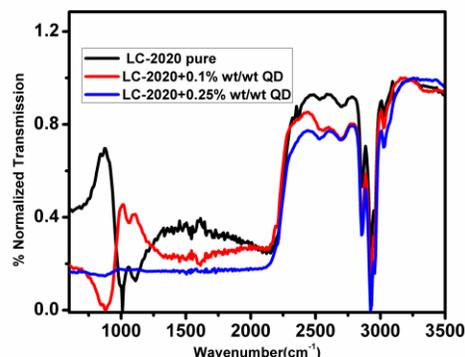
Fig.4. Graphical representation of FTIR spectra for pristine LC and QD dispersed nematic system (0.1% wt/wt and 0.25% wt/wt concentration) in transmission mode on wave number scale at 30°C

CONCLUSION

In concise, the present paper reveals the influence of QD on certain optical properties of nematic liquid crystal. The alterations in nematic liquid crystal properties are strongly dependent on the dopant concentration. A remarkable increase in UV absorbance along with the decrement in band gap and quenched Pl spectra for higher concentration of QD dispersed nematic system has been the core finding in the present investigation. The present investigation has various applications in fabrication of photovoltaic devices. Increased UV absorbance and quenched PL in QD dispersed nematic system discloses the effect of prominent interaction between aromatic rings of nematic LC molecules and QD which was also confirmed from FTIR spectra. Asymmetric and symmetric C-H stretching vibrations are confirmed from

FTIR spectra which had been the support for the quenched PL intensity. The outcome of the present investigation provides its application in the field of smart optoelectronic and photovoltaic devices.

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