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CdSe quantum dot-dispersed DOBAMBC: an electro-optical study

Swadesh Kumar Gupta[a], Dharmendra Pratap Singh[a], Pankaj Kumar Tripathi[a], Rajiv Manohar[a]*, Mahesh Varia[b], Laxmi K. Sagar[b] and Sandeep Kumar[b]

[a]*Department of Physics, Liquid Crystal Research Lab, University of Lucknow, Lucknow, India;* [b]*Soft Condensed Matter Laboratory, Raman Research Institute, Bangalore, India*

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Cadmium selenide quantum dot (CdSe QD) has been used as a dopant in ferroelectric liquid crystal (FLC) 2-methylbutyl 4-(4-decyloxybenzylideneamino) cinnamate (DOBAMBC). Effect of CdSe QD in DOBAMBC on its different electro-optical (E-O) properties has been studied in the SmC* phase. The optical micrographs recorded for the pure and composite material are showing good dispersion of QDs in the FLC matrix. Micrographs of unaligned sample cell revealed that CdSe QDs induce homeotropic alignment of FLC molecules. An appreciable change in the value of E-O parameters like tilt angle, spontaneous polarisation and response time with shifting of SmA–SmC* phase transition temperature has been observed for CdSe QD–DOBAMBC composite. The observed properties of composite system have been discussed on the basis of surface properties of QDs in FLC system.

Keywords: ferroelectric liquid crystal; quantum dots; composite system; electro-optical properties

1. Introduction

The phenomenon of ferroelectricity in liquid crystals (LCs) was first suggested by the Meyer and co-workers in chiral smectic phase [1]. The first investigated ferroelectric liquid crystal (FLC) by them was 2-methylbutyl 4-(4-decyloxybenzylideneamino) cinnamate (DOBAMBC). Further experiments by Clark and Lagerwall have shown tremendous advantages of electro-optical (E-O) properties of FLCs [2]. Later, a large number of FLCs have been investigated with fast E-O switching applicable for various practical devices [3–6]. Numerous properties of FLCs, such as spontaneous polarisation (P_s), high contrast ratio and fast E-O response, make them excellent material for displays and other applications. Ferroelectricity in the LCs is mainly governed by the coupling between P_s and tilt angle and is often termed as chiral coupling [7].

The doping of nanostructured materials has shown promising enhancement in the value of various properties of LC system. The main reason to dope these materials is to improve the E-O properties of LCs, which have shown some promising results such as high P_s, fast response and low-power operation [8–13]. Haraguchi et al. have reported the reduction of threshold voltage of twisted nematic LC devices by doping the nanoparticles of MgO and SiO_2 [10]. Mikulko et al. have shown that $BaTiO_3$ nanoparticles have significantly improved the response time of FLC mixture besides reducing the P_s [11]. Carbon nanotubes (CNTs) have also shown great aspects for the improvement of many E-O properties of LCs [12]. CNTs provide planar alignment of LC molecules, which have improved the E-O performance of LCs but form large aggregates in LC medium. Hegmann et al. discussed in their review the effect of dispersing different nanomaterials in LCs for the development of many applications in areas such as nanoscale electronics, electro-optics, sensors, optical memories and display devices [13]. Different nanoparticles have tendency to form aggregates in LC medium; this may badly influence the E-O behaviour of LCs. Therefore, it is required to assure if nanoparticles are aggregating in LC medium before using such doped system. For this purpose, a number of techniques have been used such as functionalisation and capping of nanoparticles for well-dispersed LC nanocomposite [12–14]. Out of different nanomaterials, the semiconductor nanoparticles have attracted the attention of the researchers due to their size-dependent E-O properties. In the recent few years, the quantum dots (QDs) have shown the appealing presence as a nano-scaled dopant in LCs [15–17]. Since their discovery by Alexei Ekimov in 1980s, QDs created a new field of research due to their modified semiconducting nature and fluorescent properties determined by their size [18,19].

The QDs are recently used by different scientific groups to improve various properties of LC-based devices, such as pronounced memory effect, enhanced luminescence and enhanced electrical conductivity [16–18]. Hirst et al. studied the mechanism of self-assembly of QDs in the different LC phases [17]. Mirzaei et al. also studied the threshold and

*Corresponding author. Email: rajiv.manohar@gmail.com

anisotropy behaviour of cadmium selenide (CdSe) QD-doped nematics [20]. Kinkead et al. showed that the capping agents of QDs also play an important role to affect the LC properties [14]. The QDs have also shown charge capturing phenomenon that has been retained up to many hours [21,22].

Most of the theoretical and experimental work on the FLCs was conducted on DOBAMBC initially and lot of literature is available on the pure sample [7,23,24]. Therefore, we have taken it as a host material for doping CdSe QDs. In this article, we have doped the CdSe QDs in DOBAMBC to study their effect on the performance of LC system in SmC* phase. Different E-O properties such as P_s, tilt angle and response time have been measured for the pure and doped system. It has been observed that doping of CdSe QDs in the FLC has reduced the SmC* range of the FLC sample and the values of tilt angle and P_s were also found to decrease.

2. Experimental details

In the present study, the investigated FLC material is DOBAMBC. It is a well-characterised chiral mesogenic material, and it was the first compound known to exhibit SmC* phase [1]. The material used here was obtained from the Frintron lab (Vineland, NJ, USA) and used without further purification. Its chemical structure is given in Figure 1. Its phase transition scheme is Cr 74.6°C←→(SmI* 63°C ←)←→SmC* 95°C←→SmA 117°C←→Iso. CdSe QDs stabilised by octadecylamine ligands have been used to disperse in DOBAMBC. The average size of these spherical CdSe QDs is 3.5 nm [19]. The CdSe QDs have been dispersed in concentration of 1% wt/wt ratio into the DOBAMBC. The composite was prepared by mixing the CdSe QD with DOBAMBC and then homogenised with an ultrasonic mixer for 1 h and uniform dispersion of CdSe QDs in the composite was ensured.

The E-O study of pure and CdSe QD–DOBAMBC composite have been conducted on planar geometry. The sample cells for the present study were prepared using Indium tin oxide-coated glass plates. The planar alignment was obtained by treating the conducting layer with adhesion promoter and coating it with nylon (6/6). After drying the polymer layer, substrates were rubbed unidirectionally in anti-parallel fashion. The cell thickness was maintained by placing the mylar spacer (10 μm) in between the plates and then it was sealed with UV sealant. The assembled cells were filled with sample by capillary action above the isotropic temperature of DOBAMBC.

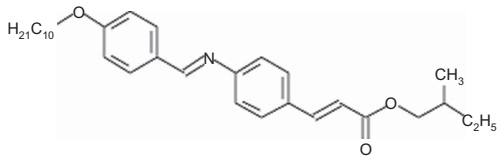

Figure 1. Molecular structure of FLC DOBAMBC.

The optical micrographs were taken using polarising microscope (RXLR-5, Radical instruments, New Delhi, India) in crossed polariser condition. The scanning electron microscope (SEM) image of QD-doped DOBAMBC was taken at room temperature, taking chloroform as a solvent with the magnification of 150 K×. The tilt angle measurement at different temperature have been studied by applying (10^4 Vcm^{-1}) square wave at 0.2 Hz of both polarities to the planar aligned sample [7]. The tilt angle was obtained by setting the two extinction position of the sample. The tilt angle is half of the angle between the two extinction positions. P_s measurement has been carried out by the polarisation current reversal method by applying triangular wave (10^4 Vcm^{-1}) at 10 Hz [7,25].

The optical response of the samples has been studied by applying 10 Hz square wave (10^4 Vcm^{-1}) to the sample cell and using a photo detector (PD02-L1, Instec, Boulder, CO, USA). The triangular and square wave pulses have been applied using a programmable function generator (AFG-3021B, Tektronix, Bangalore, India) and the optical and electrical response of the samples were recorded on a storage oscilloscope (TDS-2024C, Tektronix). The different measurement as a function of temperature have been carried out by keeping the sample on a computer-controlled hot stage (HCS-302, Instec) with an accuracy of 0.01°C. All the experiments have been carried out in the cooling cycle.

3. Result and discussion

To study the effect of octadecylamine-capped CdSe QDs in DOBAMBC, we first recorded the polarising optical microscope (POM) images. Figure 2 shows POM images of DOBAMBC and CdSe QD-doped DOBAMBC in the absence of alignment layer. It shows that QDs induced the homeotropic alignment on the FLC molecules with little to no aggregation of QDs. As the octadecylamine ligands are used for capping CdSe QDs, it adds some negative charge to the surface of QDs producing coulomb repulsion between them. This coulomb repulsion restricts the QDs to aggregate in the LC matrix. The POM image of doped sample shows uniformity in each area of texture with small aggregation. Kinkead et al. also observed the homeotropic alignment of nematic LCs by hexadecylamine-capped CdSe QDs [14]. As the

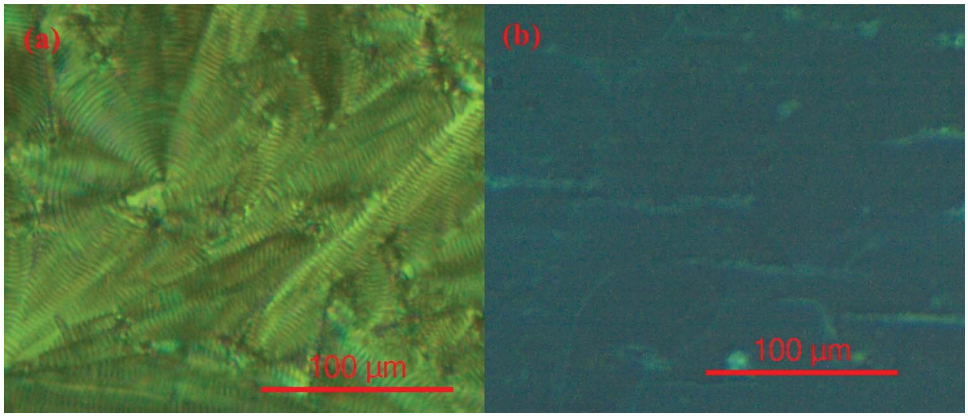

Figure 2. POM images of (a) DOBAMBC and (b) CdSe QD-doped DOBAMBC in unaligned plain glass slides under crossed polariser condition at 75°C.

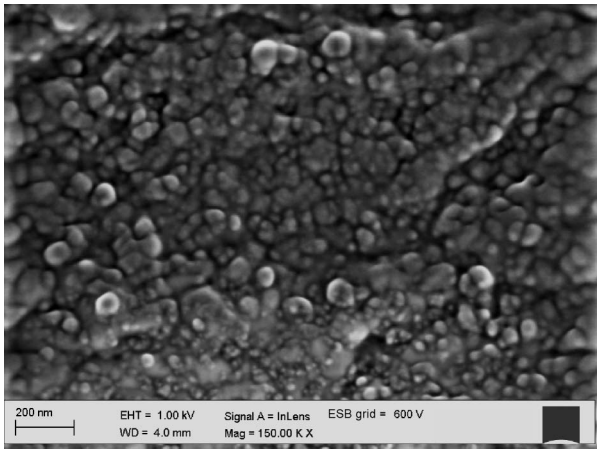

Figure 3. SEM image of CdSe QD-doped DOBAMBC at room temperature.

POM images of these unaligned samples were taken by just putting the sample on glass plate and then covered by a cover slip, the QDs show small aggregates that are not observed in planar aligned cells. The uniform dispersion of CdSe QDs in DOBAMBC has been verified by the SEM images as shown in Figure 3. The SEM image of CdSe QD-doped DOBAMBC clearly shows the uniform dispersion of QDs in the FLC system.

Unlike the unaligned samples, POM images of QD-doped DOBAMBC in planar aligned cells show homogeneous planar alignment with no visible aggregation as shown in the Figure 4. At first sight, it suggests that the aligning ability of QDs is not strong enough to overcome the surface effect of the alignment layer. As DOBAMBC is a short-pitch material (~2 μm), it becomes unfeasible to make uniformly aligned sample. Therefore, a number of different bright lines are observed in dark state of pure DOBAMBC (Figure 4(b)). It can be seen from Figure 4(d) that the doping of CdSe QDs shows the uniform dark state of DOBAMBC with less bright lines than to pure DOBAMBC. It indicates that although the QDs are not showing the homeotropic alignment of FLC molecules in planar aligned cells, QDs are inducing some pretilt of FLC molecules in the layers away from the aligned glass substrate.

Figure 5 shows the variation of tilt angle (θ) with the temperature for the pure and CdSe QD-doped DOBAMBC in ferroelectric phase. It was observed that the addition of QDs has decreased the value of tilt angle. This decrement in the tilt angle can be understood on the basis of the interaction between CdSe QD and FLC molecule. Therefore, as the QDs show charge capturing phenomenon, the charge transfer from dipolar –C = O group of DOBAMBC molecule to surface of semiconductor QDs creates an electron donor–acceptor interaction between them. Therefore, the interaction between QDs and FLC molecule tries to reduce the helical tilt angle. In addition, the value of tilt angle for doped system diminished well before the SmC*–SmA transition temperature (T_c) of DOBAMBC. It indicates that the transition temperature has been decreased with addition of CdSe QDs.

In planar aligned cell, the FLC molecules point to almost same direction. When the QDs are doped they disrupt the molecular ordering by incorporating themselves between the group of molecules and smectic plane and induce pretilt in the molecules. Therefore, the addition of QDs provides a less-ordered system causing a decrease in transition temperature T_c. The change in the transition temperature for different FLC composites has already been reported by our group [4–6].

Figure 6 shows the behaviour of P_s with variation of temperature for the pure and CdSe QD-doped

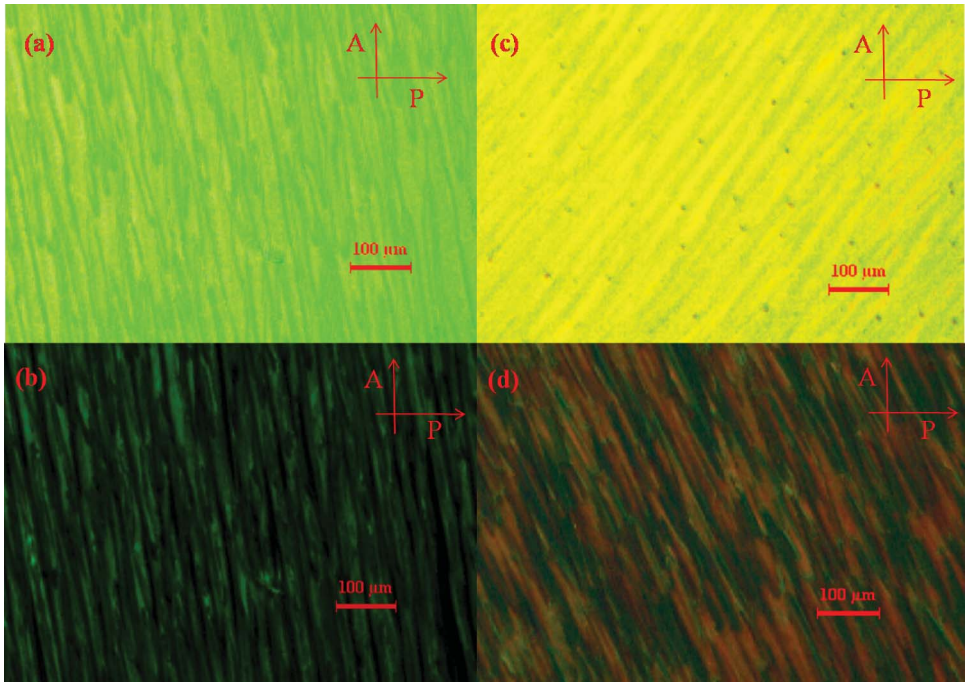

Figure 4. POM images of DOBAMBC material doped with 0% and 1% wt/wt CdSe QDs (a), (c) bright states and (b), (d) dark state at 75°C, respectively. The bright and dark state has been taken by rotating the sample cell under polarising microscope under crossed polariser condition.

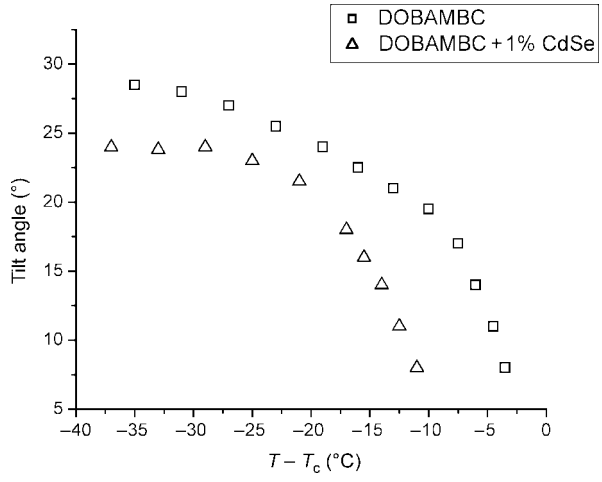

Figure 5. Variation in the value of tilt angle (θ) as a function of reduced temperature for pure and 1% CdSe QD-doped DOBAMBC. A square wave of 20 Vpp has been applied at 0.2 Hz. (Reduced temperature has been taken relative to SmA–SmC* transition temperature of pure DOBAMBC and the same is used in other figures.)

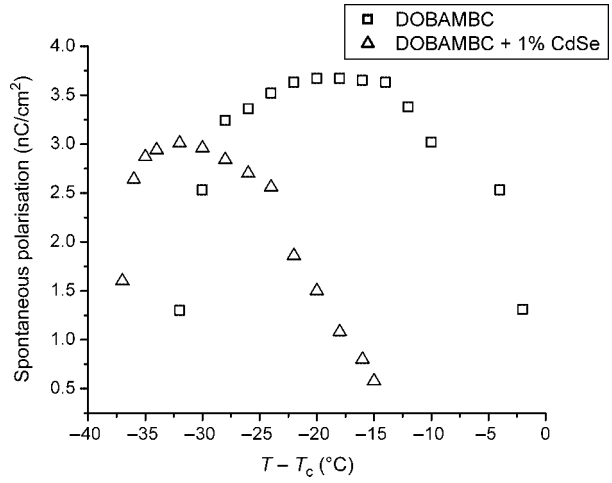

Figure 6. Spontaneous polarisation versus temperature for pure and 1% CdSe QD-doped DOBAMBC. A triangular wave of 20 Vpp at 10 Hz has been applied for electrical response.

DOBAMBC. The maximum value of P_s has been decreased and shifted to reduce temperature for CdSe QD-doped DOBAMBC. A sharp decrease in the value of P_s after attaining its maximum value suggests that although the rotation of chiral centre is hindered near the transition to SmI* phase, the motion of dipolar –C = O group can remain synchronised with this rotation [26]. In the FLC, the value of P_s is directly coupled with the tilt angle of the FLC molecule. This decrease in the value of P_s can be attributed to the lowering of tilt angle, as the value of tilt angle has been decreased for CdSe QD-doped DOBAMBC.

The P_s in FLCs depends upon the normal component of dipole moment of molecules. Figure 6 clearly shows that the complete SmC* phase has been shifted to lower temperature side for CdSe QD-doped DOBAMBC accompanied with a reduction in the P_s. This means that there may be some factor other than tilt angle involved for such a shifting and decrease of P_s in the CdSe QD-doped DOBAMBC. Therefore, as already discussed that CdSe QDs are providing a pretilt in the FLC system, total dipolar contribution to the normal component get reduced causing small value of P_s in CdSe QD-doped DOBAMBC.

The decrease in the value of P_s for CdSe-doped DOBAMBC suggests the slower response of molecules to the applied electric field. Optical response time for pure and CdSe QD-doped DOBAMBC has also been studied with the variation of temperature as shown in Figure 7. Response time for CdSe QD-doped DOBAMBC has been increased upto 2 times when compared with DOBAMBC. At low temperatures near SmC*–SmI transition, the decrease in the value of response time with decreasing temperature for doped FLC system is also observed due to the small fluctuation of dipolar group as discussed above. After this, a sharp decrease is observed with increasing temperature, which becomes nearly constant at higher temperatures.

The observed behaviour of response time is due to the combined effect of P_s and rotational viscosity of the pure and doped FLC system. The rotational viscosity has been calculated at different temperatures using the equation $P_s = \gamma_d/\tau$. E, where τ is the optical response time and E is the applied electric field [7]. From the behaviour of rotational viscosity shown in Figure 8, it can be observed that its value has been

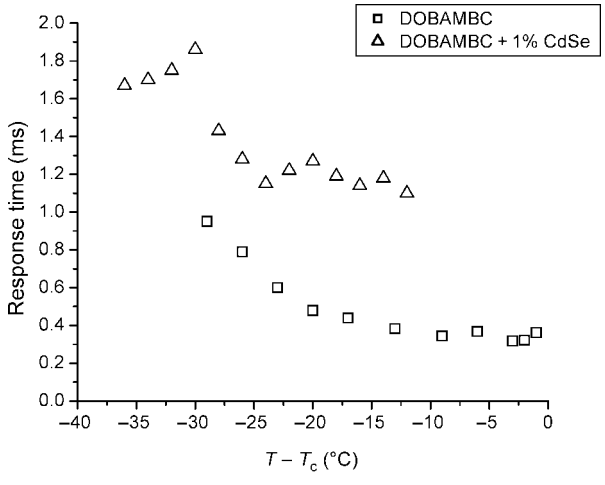

Figure 7. Response time for pure and 1% CdSe QD-doped DOBAMBC with variation of temperature. A square wave of 20 Vpp at 10 Hz has been applied for optical response.

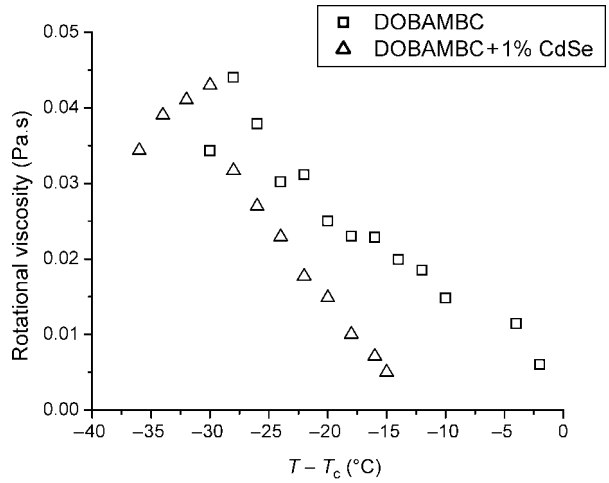

Figure 8. Rotational viscosity as a function of temperature for pure and 1% CdSe QD-doped DOBAMBC in SmC* phase.

decreased with the doping of CdSe QDs. The value of rotational viscosity is nearly the same for the composite as compared to the pure DOBAMBC and then sharp decrease is observed on further increase in the temperature. Therefore, the increase in response time for CdSe–DOBAMBC composite is clearly a consequence of decrease in the P_s and dominates over the decrease in the value of rotational viscosity. Mikulko et al. also reported the decrease in rotational viscosity with addition of $BaTiO_3$ nanoparticles in FLC mixture [11].

This slight decrement in the value of rotational viscosity with the doping of CdSe QDs indicates that the interaction between QD particle and FLC molecule is not hindering the motion of FLC molecules. Since the Goldstone mode of relaxation in the FLCs is due to the phase fluctuation of molecules, the zth component of rotational viscosity is the active component of γ_d, which gets reduced due to the pretilt induced by CdSe QDs. A decrease in the value of rotational viscosity at low temperatures suggests that the switching at lower temperatures is not due to the complete rotation of FLC molecules but a small fluctuation of dipolar group near SmC*–SmI* transition is responsible for such a decrease in rotational viscosity.

4. Conclusion

In summary, we have explored the effect of doping octadecylamine-capped CdSe QDs in DOBAMBC. From the study of optical micrographs of CdSe QD-doped DOBAMBC, we observed that QDs induce the homeotropic alignment of FLC molecules in unaligned sample with small aggregation. The SEM

image has also shown the uniform dispersion of QDs in FLC system. In planar aligned cell, these QDs induce only some pretilt on the FLC molecules rather than changing them to complete homeotropic alignment. This pretilt greatly influences the E-O properties and transition temperature of the composite. The E-O behaviour of composite shows a decrease in the value of tilt angle and P_s with slower response of FLC molecules. As the doping of CdSe QDs brings down the transition temperature of LC, the system can be used to further down the transition temperature of SmC* phase. Therefore, it may be interesting to dope some other type of nanoparticle or CNTs in the present system to optimise its E-O properties.

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