PHYSICAL REVIEW E **80**, 010701(R) (2009)

Evidence for directed self-assembly of quantum dots in a nematic liquid crystal

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(Received 27 January 2009; published 22 July 2009)

Assembling quantum dots (QDs) into nanoscale configurations over macroscopic dimensions is an important goal to realizing their electro-optical potential. In this Rapid Communication, we present a detailed study of a pentylcyanobiphenyl liquid crystal (LC) and a CdS QD colloidal dispersion by probing the dielectric property $\bar{\varepsilon}$ and relaxation as a function of an applied ac electric field E_{ac}. In principle, dispersing QDs in a nematic LC medium can direct the dots to align in nearly one-dimensional chainlike structures along the nematic director and these assemblies of QDs can be directed by external electric fields. In a uniform planar aligned cell, the Fréedericksz switching of the LC+QDs appears as a two-step process with the same initial switching field as the bulk but with the final $\bar{\varepsilon}$ value larger than that for an aligned bulk LC. The relaxation of $\bar{\varepsilon}$ immediately following the removal of E_{ac} follows a single-exponential decay to its original value that is slower than the bulk but becomes progressively faster with increasing E_{ac}, eventually saturating. These results suggest that the arrangement of the QDs is mediated by the LC.

DOI: 10.1103/PhysRevE.80.010701 PACS number(s): 77.84.Nh, 73.21.La

Controlled self-assembly of semiconductor quantum dots (QDs) holds great promise for numerous applications, such as next generation photonic devices, QD displays, biomedical imaging [1–9], and, perhaps, solid-state quantum computation. Electrochemical self-assembly of QDs on a chosen substrate is one of the most efficient techniques to form highly ordered QD aggregates. However, this technique, such as others, does not allow manipulating the QD aggregates in a preferred direction after the completion of the self-assembly process. Recently, it has been demonstrated that nanomaterials such as nanotubes or nanorods can be organized by nematic *liquid crystals* (LCs) [10–12]. In this case, the anisotropic order of the LC imparts order onto the nanosize guest particles, along the *nematic director* (average orientational direction of the LC molecules), for example, due to the reduction in excluded volume [13]. Because the director can be aligned by external electric fields, the nanoscale assemblies of the QDs in the LC can be manipulated. Recent research shows that smectic LC environment allows QDs to achieve high spatial ordering into quasi-one-dimensional arrays along the director [14]. Understanding the interaction of nanoparticles with an LC and the principles governing their assembly through an LC mediated interactions is an important and active area of research.

The nematic phase shows dielectric anisotropy due to the anisotropic nature of the LC molecules where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the components parallel and perpendicular to the molecular long axis, respectively. For a positive dielectric anisotropic LC, $\varepsilon_{\parallel} > \varepsilon_{\perp}$ and so reorients to align the molecular long axis (nematic director for the whole ensemble) parallel to an applied electric field. In a uniform homogeneously aligned parallel-plate cell configuration, the nematic director is aligned perpendicular to the applied electric field due to surface anchoring but the director can reorient parallel to E_{ac} if the field magnitude is above some critical threshold. This is the essence of a Fréedericksz transition and an ac capacitive measurement of the $\bar{\varepsilon}$ will reveal $\varepsilon_{\perp}$ below and $\varepsilon_{\parallel}$ above this switching, the exact values depending on frequency. The dispersion of spherical particles having an isotropic $\bar{\varepsilon}$, such as CdS quantum dots, typically introduces random surfaces that disrupt the uniform nematic alignment. Thus, for such LC colloids, intermediate values of $\bar{\varepsilon}$ are observed but with a constant offset proportional to the amount of the spherical particles.

It has been shown that to minimize elastic distortions in the LC, micrometer size spherical particles tends to be distributed into cylindrically symmetric chain or strands along the global nematic director, which is essential a minimization of excluded volume [13,15]. However, it is not clear how this analysis would change or remain valid as the spherical particles diameter is reduced to nanometer scales, such as QDs.

In this Rapid Communication, we report the dielectric constant $\bar{\varepsilon}$ and its relaxation as a function of the magnitude of an applied ac electric field E_{ac} for a colloidal dispersion of cadmium sulfide (CdS) QDs in the nematic 4-cyano-4′-pentylbiphenyl (5CB), denoted as LC+QD, inside a homogeneously aligned planar cell. With increasing E_{ac}, $\bar{\varepsilon}$ reveals a Fréedericksz reorientation transition for the LC+QD sample that initiates at the same E_{ac} as the bulk LC but exhibits a second step at a higher E_{ac}, finally saturating at a value of $\bar{\varepsilon}$ larger than that for the bulk. For the relaxation study on switching E_{ac} off, the LC+QD system relaxes through a single-exponential decay back to a planar orientation, recovering the original value of $\bar{\varepsilon}$ prior to the application of E_{ac}. The relaxation time is larger for the LC+QD system than bulk 5CB but both saturate to a relaxation time above the same E_{ac}. We present a physical interpretation to explain these results that proposes the QDs arranged in "pearl-necklace" strands, held together by LC mediated interactions, that do not rotate as a single structure but reassembles along the new orientation axis—hence, directed self-assembly.

Our LC+QD sample consisted of a small amount (1 wt %) of CdS quantum dots (UV absorption peak: 361 nm and diameter of 2.3 nm in toluene solvent) [16] dispersed

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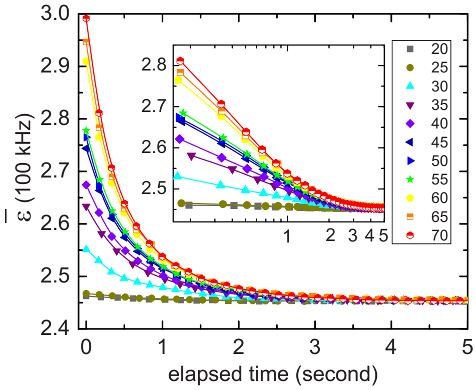

FIG. 1. (Color online) Dynamic response of the average dielectric constant $\bar{\varepsilon}$ for the 5CB+CdS system in the nematic phase ($T=25$ °C) after $E_{ac}=0$. The inset (same main graph axes) represents the same relaxation in logarithmic time scale to show the single exponential decay. The lines represent the fitting according to a single exponential decay function, see text for details. The legend represents the magnitude of E_{ac} (1 MHz) in kV/m.

in 5CB (the isotropic to nematic transition at $T_{IN}=35$ °C). The LC+QD+solvent mixture was ultrasonicated for 5 h to achieve a uniform dispersion. The mixture was then heated to just above T_{IN} to evaporate the toluene slowly followed by degassing under vacuum for 2 h. The LC+QD mixture was then filled into an electro-optical cell [5×5 mm^2 indium tin oxide (ITO) coated area and 20 μm spacing] [17] by capillary action. The patterned-electrode surface inside the LC cell imposes the uniform planar alignment to the nematic director. A homemade ac capacitive dielectric spectrometer [18–21] was used to measure $\bar{\varepsilon}$ as a function of an applied ac electric field E_{ac}, to avoid ion migration, as well as time following the removal of E_{ac}. All measurements were performed isothermally at $T=25$ °C, deep in the nematic phase. An empty cell was also measured in order to extract the absolute $\bar{\varepsilon}$ value, and an identical cell arrangement was used for pure bulk 5CB and empty in order to make quantitative comparisons to the 5CB+CdS sample.

After the 5CB+CdS sample was loaded into the cell, an external ac electric field pulse, E_{ac} (1 MHz of 30 s duration) was applied across the cell at magnitudes ranging from 0–250 kV/m and $\bar{\varepsilon}$ measured. Following each measurement at a given E_{ac}, a relaxation study was performed by turning off the electric field (at $t=0$ s) and monitoring $\bar{\varepsilon}$ as a function of time. Once fully relaxed, the next higher value of E_{ac} was applied and the sequence repeated. Figure 1 shows the decay of $\bar{\varepsilon}$ (t) for each value of E_{ac} for the 5CB+QD sample. Figure 2 shows $\bar{\varepsilon}$ ($t=0^-$), the value of $\bar{\varepsilon}$ just before E_{ac} is removed for 5CB+QDs and bulk 5CB samples. Note that our dielectric measurements were performed using a probing field far below the reorientation threshold field and at frequency (100 kHz) far below that for E_{ac}.

Field-induced director orientation occurs when the torques due to the external electric field overcome the elastic interactions between LC molecules, and being embedded in the LC matrix, one-dimensional QD chains coupled with the director follow the director reorientation. Soon after the field goes off, these restoring forces, between the planar surface state and LC director, drive the system (LC+QD arrays) back to the original state. Figure 1 shows the average dielectric constant, $\bar{\varepsilon}$ (measured at 100 kHz) as a function of time after E_{ac} was tuned off for the 5CB+CdS sample. In the nematic phase ($T=25$ °C), QD arrays and LC molecules cooperatively relax back to the planar orientation after the field goes off. The field-saturated dielectric constant, $\bar{\varepsilon}_{max}$ ($\bar{\varepsilon}$ at $t=0$, from Fig. 1) for each relaxation is plotted as a function of E_{ac} in Fig. 2(a) and is directly associated with the director orientation. The value of $\bar{\varepsilon}_{max}$ starts to increase above $E_{ac}=20$ kV/m for both pure 5CB and 5CB+CdS samples, confirming the director reorientation from planar to homeotropic. The saturation for $\bar{\varepsilon}_{max}$ above $E_{ac}=80$ kV/m demonstrates the complete homeotropic alignment (tilt angle=90°) of the LC director and the coupled QD chains in the cell. Before the field-induced reorientation for the LC+QD system, one-dimensional QD arrays, being perpendicular to the measuring field, contribute their average $\varepsilon_\perp$ to the average dielectric constant of the system. Figure 2(a) shows that the average dielectric constant of the composite system increases by an amount $\Delta\varepsilon_1=0.08$. After the saturation point, when the system is fully reoriented parallel to the field, QD arrays also show homeotropic alignment, contributing their average $\varepsilon_\parallel$ ($>\varepsilon_\perp$) to the system. The difference in $\bar{\varepsilon}_{max}$ between pure 5CB and 5CB+CdS after the saturation is given by $\Delta\varepsilon_2=0.15$ (87.5% increase), shown in Fig. 2(a). The significant dielectric difference $\Delta\varepsilon=\Delta\varepsilon_2-\Delta\varepsilon_1=0.07$ due to the presence of only 1 wt % of QDs in LC media suggests that the spherical QDs form highly anisotropic structures along the director. This is consistent with the view that the anisotropic cylindri-

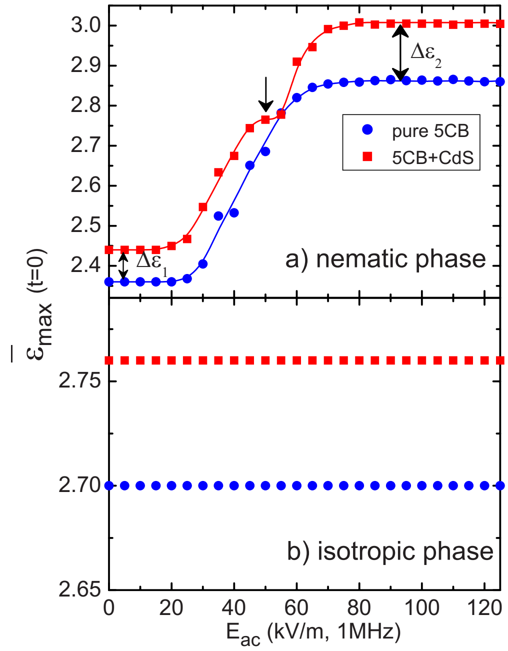

FIG. 2. (Color online) (a) Field-saturated dielectric constant, $\bar{\varepsilon}_{max}$ ($\bar{\varepsilon}$ at $t=0$) as a function E_{ac} for pure 5CB and 5CB+CdS in the nematic phase ($T=25$ °C). The downward arrow indicates the intermediate step for 5CB+CdS. Lines represent guide to the eyes; (b) Field-saturated dielectric constant, $\bar{\varepsilon}_{max}$ ($\bar{\varepsilon}$ at $t=0$) as a function E_{ac} for pure 5CB and 5CB+CdS in the isotropic phase ($T=45$ °C)

cally symmetric nematic environment favors a cylindrically symmetric arrangement of the QDs, i.e., essentially one-dimensional QD arrays or chains. If the QDs were to stay in the LC matrix without forming the arrays, one would expect $\Delta\varepsilon_1$ to be equal to $\Delta\varepsilon_2$. At each given field-induced director reorientation, QDs could form new chains keeping the average length and numbers of the chains roughly constant. At each magnitude of an applied electric field, the previously formed QD chains could be deformed due to the nematic director coupling inducing mechanical torques. After completion of each director rotation, the QDs reassemble to construct new chains. The intermediate step found in $\bar{\varepsilon}_{\max}$ [Fig. 2(a)] for 5CB+CdS system indicates that the presence of a small amount of QDs induces local random disorders in the nematic media. A strong enough E_{ac} allows the system to improve nematic ordering, compensating the disorder effect. This field-induced improved nematic order enhances the self-assembly of QDs, resulting in an increase in $\bar{\varepsilon}_{\max}$ with further increasing E_{ac} above this intermediate step.

The same experiment was repeated in the isotropic phase ($T=45\ ^\circ\mathrm{C}$). Due to the absence of the nematic mediated (elastic) interactions in the isotropic phase, it is expected that there should be no field-induced director reorientation for pure 5CB in the isotropic phase as confirmed in Fig. 2(b). The value of $\bar{\varepsilon}_{\max}$ of the 5CB+QD system in the isotropic phase does not change with increasing E_{ac}, indicating that the QDs are probably homogeneously distributed and do not form self-assembled arrays, see Fig. 2(b). In addition, the dielectric constant of the CdS solution (2 mg/cc in toluene) under the same experimental condition does not depend on E_{ac}, confirming that the CdS nanocrystals in bulk solution are not field responsive to form anisotropic arrays.

The relaxation dynamics of 5CB or the QDs cannot be separated from the dielectric relaxation in these studies, including at the intermediated step near $E_{ac}=50\ \mathrm{kV/m}$. Only a single exponential relaxation is observed as seen in Fig. 1, the semilogarithmic inset in Fig. 1. The dielectric relaxation curves for 5CB and 5CB+CdS composite were well fitted according to a single-exponential decay function $f(t)=\bar{\varepsilon}_1 e^{(-t/\tau)}+\bar{\varepsilon}_0$, with a typical regression coefficient of $R=0.9976$. Here, τ is the relaxation decay time, $\bar{\varepsilon}_0$ is the average base dielectric constant, and $\bar{\varepsilon}_1$ is the field-induced average dielectric constant. Thus, the field-saturated average dielectric constant, $\bar{\varepsilon}_{\max}=\bar{\varepsilon}_0+\bar{\varepsilon}_1$. The values for the three fitting parameters, τ, $\bar{\varepsilon}_0$, and $\bar{\varepsilon}_1$ as a function of E_{ac} are shown in Fig. 3. The relaxation time for pure 5CB and 5CB+CdS decreases as E_{ac} increases and saturates at a higher field, which is consistent with the behaviors of $\bar{\varepsilon}_{\max}$ shown in Fig. 2(a). For E_{ac} larger than the saturation point, the composite system relaxes back slower than pure 5CB. It is possible that the presence of QD-arrays increases the mean viscosity and allows the system to relax slower but the low fixed concentration used seems unlikely without the self-assembled arrays having significant asymmetry. A cylindrically assembled array of QDs would affect the rotational viscosity more effectively and so more directly alter the dielectric relaxation. Additional measurements with the slightly larger dots (diameter 3.6 nm and 1.36 wt % in LC) yielded longer relaxation times ($\tau=0.52\ \mathrm{s}$), indication that larger the anisotropy longer the relaxation dynamics. The fitting parameter, $\bar{\varepsilon}_1$, tracks the behavior of the observed $\bar{\varepsilon}_{\max}$ for pure 5CB and 5CB+CdS, indicating self-consistency. The difference in $\bar{\varepsilon}_1$ between 5CB and 5CB+CdS after the saturation point is $\Delta\varepsilon=0.0698$. See Fig. 3. This value of $\Delta\varepsilon$ has been found to be very close to the value of $\Delta\varepsilon_2-\Delta\varepsilon_1$ from Fig. 2(a).

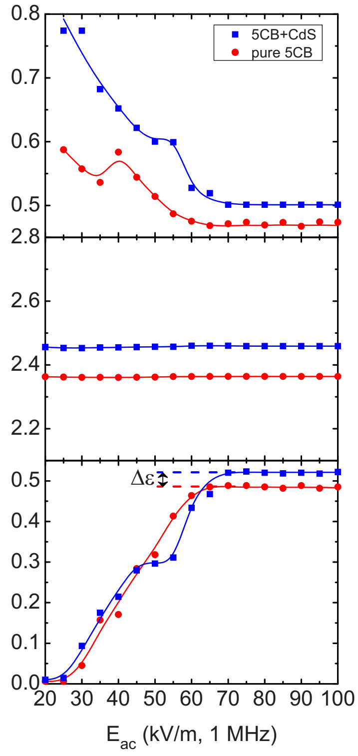

FIG. 3. (Color online) Fitting parameters according to a single-exponential decay $(f(t)=\bar{\varepsilon}_1 e^{(-t/\tau)}+\bar{\varepsilon}_0)$ function for pure 5CB and 5CB+CdS system. Lines represent guide to the eyes.

Optical cross-polarizing microscopy studies on the same

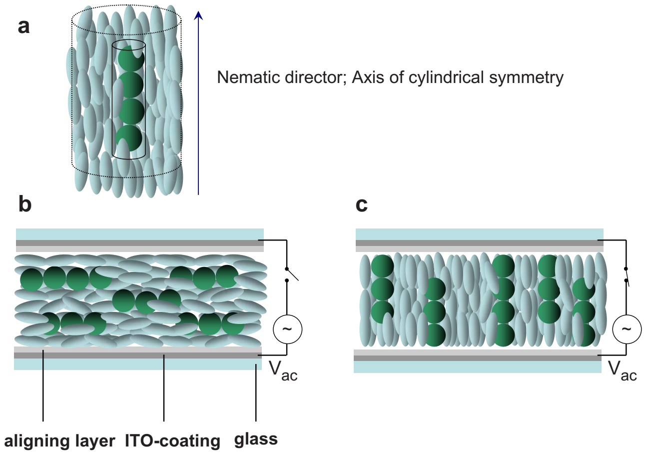

FIG. 4. (Color online) Schematic diagrams; (a) dotted cylinder shows the cylindrical symmetry of uniaxial nematic phase; the small cylinder shows the cylindrical confinement of self-assembled QDs aggregation; (b) electrode-surface-induced homogeneous alignment of nematic LC molecules (ellipsoidal), and QD self-assembly (spherical) in the nematic matrix; (c) electric field-induced homeotropic alignment of nematic LC molecules, and homeotropically directed one-dimensional QD arrays.

sample of 5CB+QD was attempted. The micrographs reveal a uniform texture indicating a uniform nematic director field. No indicates of phase separation or large scale agglomerates were observed at any temperature. Thus, at least on the length scales probed by visible light, the arrangements of the QD must be small structures due to their low concentration and uniformly distributed. More detailed optical and x-ray studies would be of great benefit to directly probe the local QD assemblies.

A rough estimation of number of QD chains and number of QDs in a chain can be made based on the following simple model. For the QD chains, as explained earlier, the *homogeneous* configuration contributes $\varepsilon_{\|}$ and the *homeotropic* configuration contributes $\varepsilon_{\perp}$ to the average dielectric constant of the host system, $\Delta\varepsilon=\varepsilon_{\|}-\varepsilon_{\perp}$. Quantum dots were initially dispersed isotropically in toluene solvent. One can extract the average contribution, $\delta\varepsilon_0$, of QDs to the dielectric constant of any isotropic media once the average dielectric constants for the QD+toluene sample and pure toluene are known. If n is the number of QDs in a chain, then one can write $\Delta\varepsilon \cong n\delta\varepsilon_0-\delta\varepsilon_0$ or $n=(\Delta\varepsilon/\delta\varepsilon_0)-1\approx 2000$ using the dielectric values measured here. The total number of QDs in the 5CB+QD sample within the capacitive cell is known to be roughly $N\approx 70\times 10^{12}$, and so the total number of chains is approximately $m=n/N=35\times 10^{9}$. This is small compared to the total number of 5CB molecules, but their arrangement into LC+field aligned chains can significantly influence the measured dielectric constant. See Fig. 4.

In summary, the dynamics of 5CB+CdS system has been probed by studying average dielectric response to understand the stability of this system. The results clearly demonstrate that the nematic phase imposes self-assembly on QDs to form one-dimensional arrays. An application of electric field can direct the axis of the self-aggregation in a preferred orientation direction as illustrated in Fig. 4. This is consistent with the behavior in the isotropic phase being independent of E_{ac}, and the enhanced $\bar{\varepsilon}$ above $E_{\mathrm{ac}}=50$ kV/m, indicating that only the nematic phase of LC induces this self-assembly on CdS nanocrystals. This Rapid Communication opens up future theoretical and experimental studies to get precise information on structures of QD arrays. Future work involves optoelectric studies of field-induced fluorescence spectra for different sizes of QDs in nematic LC media.

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