Effect of two different size chiral ligand-capped gold nanoparticle dopants on the electro-optic and dielectric dynamics of a ferroelectric liquid crystal mixture

R. K. Shukla, A. Sharma, T. Mori, T. Hegmann and W. Haase

ABSTRACT

Nanocolloids consisting of a ferroelectric liquid crystal (FLC) doped with different concentrations (0.10 and 0.50 wt.%) of surface treated gold nanoparticles (GNPs) differing in size (1.77, 5.5 nm) are prepared and characterised. The effects of doping on the clearing temperatures as well as electro-optic and dielectric parameters of a FLC mixture are presented. The clearing temperatures remain invariant with doping. A remarkable increase in the spontaneous polarisation is noticed due to the addition of the GNPs with chiral monolayer capping. Tilt angle and switching time, at least in their tendency, become slightly reduced and increased, respectively. Depending on the size of the nanoparticles, surface plasmon resonance is observed to be slightly increased by increasing the surface. In addition, a small change in localised electric field is found upon doping. The increase in the dielectric permittivity and the dielectric strength is observed and attributed to the parallel coupling between the dipoles of functionalised GNPs, induced by external electric field, and the vector of the spontaneous polarisation of the FLC matrix. A decrease in relaxation frequency is observed. A substantial increment of one order in the dc conductivity is also observed for the nanocolloids.

INTRODUCTION

In the recent past, liquid crystals (LCs) emerged as a promising anisotropic fluidic host to assemble nanoparticles into a variety of mesoscopic architectures. Such mesoscopic architectures gained much attention due to the unusual effects of their long-range ordering on the optoelectronic and physical properties. Because of the long-range ordering of the LCs, the dispersed nanoparticles can be organised in a variety of ways depending on the choice of external stimuli, the shape anisotropy (e.g. nanorods), the particle size and perhaps most importantly the surface.
The addition of distinct size nanoscale dopants, such as nanoparticles and nanorods with gold, semiconductor quantum dot, metal oxide (ferroelectric and magnetic) cores or carbon-based nanomaterials such as nanotubes into diverse LCs (nematic and ferroelectric) has been reported in the recent past.[1] Among those, gold nanoparticles (GNPs) are considered versatile dopants as they show size-dependent electronic, optical and chemical properties due to the quantum confinement of free electrons compared to the bulk gold metal.[2] The absorption of visible light by GNPs reveals that there is a collective oscillation of free electrons, owing to the strong interactions of the incident electromagnetic field with the free-electron cloud at the surface of the GNPs. Surface plasmon resonance (SPR) is result of such collective free electron oscillations. The SPR depends on the size, shape and dielectric constant of the GNP and the host matrix.[3–6]

Thus far, GNPs and gold nanorods (GNRs) of diverse shape and size, bare or capped with functional ligands have been dispersed in ferroelectric liquid crystals (FLC) and explored for display and non-display applications. The surface functionalisation with suitable capping agent is significant as it prevents the agglomeration of nanoparticles, enhances the miscibility of the nanoscale dopant in the LC host and enhances the stability of the final LC nanocolloids.[1,7]

For GNP–FLC nanocolloids, one of the first reports is published by Kaur et al. in 2006. They highlight a significant alteration of various FLC parameters upon GNP doping including a five-fold increase in optical tilt and a large enhancement in memory effect.[8] In another report, Prakash et al. [9] investigated the effects of citrate-capped GNP doping in deformed helix ferroelectric LCs (DHFLCs) and describe a long-lasting non-volatile memory effect. In addition, a nine-fold enhancement in the photoluminescence intensity was reported for the GNPs–DHFLC mixture by Kumar and co-workers.[10] Podgornov et al. [11] investigated the size-dependent influence of polymer-capped GNPs on the electro-optical and dielectric properties of FLCs. A significant decrease in the spontaneous polarisation, the switching time as well as the rotational viscosity was reported, while the tilt angle remained invariant with GNP doping. In 2010, Joshi et al. [12] described a low-frequency relaxation mode in the SmC* phase of GNP-doped FLC composites. The influence of the chain length and tethered LC functional groups of dispersed GNPs on the electro-optical and dielectric properties of GNP–FLC nanocolloids was reported by Lapanik et al. in 2012.[13] The switching time, the rotational viscosity and the spontaneous polarisation of the nanocolloids were found to be decreased with increasing concentration of the GNPs. Longer alkyl chain-capped GNPs, likely because of their enhanced miscibility in the FLC matrix, favoured a reduction of these parameters. Here, the increase in alkyl chain length can be correlated with reduced internal repulsion among nanoparticles. Recently, we also reported on GNR–FLC nanocolloids where the GNPs were functionalised with mesogenic ligands.[14] In this particular system, the measured electro-optic parameters showed a significant modulation upon doping with these LC-functionalised GNRs. Very recently, Hegmann and co-workers demonstrated effective chirality transfer of chiral LC ligand-capped nanoparticles to bulk nematic LCs. Clear trends were established between the helical pitch of the induced chiral nematic (N*) phase and the nanoparticle size as well as number of chiral ligands attached to the surface of the nanoparticles.[15]

Considering all these results, the present study is devoted to explore the doping effects of GNPs of different size capped with chiral cholesterol-thiolates on a FLC matrix. The key foci of this study are to investigate the effects of GNP size, the length of the aliphatic tether between the GNP surface and the chiral ligand on the electro-optic and dielectric parameters of the host FLC mixture. We also examined the effects of localised electric fields and ion capturing in these GNPs–FLC nanocolloids. The obtained results are then compared with data available from existing reports on GNP and GNR–FLC nanocolloids. The comparative study is based on the parameters such as shape and size of particles, nature of the capping ligand and the chain lengths of the aliphatic segments separating the NP core from the functional group interacting with the FLC host molecules.

**Materials and methods**

GNPs with distinct sizes and functional groups were used in this study. The synthesis of the cholesterol-thiolate functionalised GNPs **NP1** (n = 6) and **NP2** (n = 11) was described earlier.[15] The chemical structures and size information for NP1 and NP2 are provided in Figure 1. **NP1** with 1.77 nm in diameter is surrounded by about 45 cholesterol-thiolate groups, **NP2** with diameter 5.5 nm showed ca. 450 such groups at the gold surface. Visible absorption spectra of both GNPs in toluene were recorded using a dual-cell OLIS14 Clarity spectrophotometer. High-resolution transmission electron microscopy analysis was performed with a FEI Tecnai TF20 TEM instrument at an accelerating voltage of 200 kV. Samples were prepared by evaporating a drop of dilute GNP solution in toluene onto carbon-coated copper TEM grids (400-mesh) and dried overnight.
The functionalised GNPs were dispersed in \( n \)-hexane and sonicated until homogenous solutions were achieved (examined visually). The nanocolloids were prepared by adding the appropriate amount of the nanoparticles NP1 and NP2 dispersed in \( n \)-hexane in the FLC host material. In the present study, two concentrations (0.1 and 0.5 wt.%) of the two NPs were prepared. The \( n \)-hexane solvent was then evaporated by slow heating of the colloidal mixtures. The non-doped FLC mixture used in present study was comprised of phenylpyrimidines and has a phase sequence 25.0°C–SmC*–65.4°C–SmA*–69.8°C–Iso (onset of the SmC* phase may be at <25.0°C). The components of the FLC are as follows:

\[
\text{C}_5\text{H}_{2n+1}-\text{N} \quad \text{OC}_m\text{H}_{2m+1} \\
\text{C}_n\text{H}_m-\text{OCOCH}_3 \quad \text{C}_5\text{H}_{11} \quad \text{OCO} \\
\]

The first kind of molecules leads to a smectic C mixture with weight concentrations for \( m = 8, n = 10 \) of 43.3%, \( m = 9, n = 8 \) of 33.3% and \( m = 8, n = 8 \) of 23.4%. A terphenyl-based chiral dopant (second molecule, non-liquid crystalline) was used for the preparation of the FLC mixture, having two chiral \( \text{C}_5\text{H}_{11}\text{CH}^+ \) (CH\(_3\))–OCO groups in the \( p, p' \) positions. The ratio of mesogenic compounds and chiral dopant in the FLC mixture was 75:25 wt.%. The non-doped FLC and the as-prepared nanocolloids were filled in planar aligned cells with a cell gap of 3.5 \( \mu \)m in separate experiments. The planar alignment was achieved by a unidirectional rubbed (50 times) nylon-6 polymer coating.

Textural variations and clearing temperatures of the non-doped FLC and the LC nanocolloids were observed at 100\( \times \) in transmission mode between crossed polarisers using convergent white light illumination of an Orthoplan Pol polarising microscope equipped with a digital camera and a Linkam LTS 350 heating/cooling stage. Temperatures measurement accuracy was ±0.5°C.

A set-up consisting of a He–Ne laser (\( \lambda = 632.8 \) nm) rotating table, Linkam LTS 350 heating/cooling stage coupled with the temperature controller Linkam CI 94 (with an accuracy ±0.1°C), function generator HP 33120A, and the digital oscilloscope HP Infinium was used to obtain the electro-optic parameters. The magnitude of the bipolar rectangular electric field and frequency were fixed about 10 V/\( \mu \)m and 3 Hz, respectively, for electro-optic measurements of the non-doped FLC and the LC nanocolloids. The saturation field observed for the non-doped FLC and the LC nanocolloids was well below that field strength. The spontaneous polarisation was measured using the well-known reverse current technique using a triangular waveform of the applied voltage [16] by applying the saturated field strength of 15 V/\( \mu \)m. Accuracy of such...
measurements was ±1 nC/cm², while the accuracy for the switching time and the optical tilt was ±1 µs and ±1°, respectively. Dielectric measurements were carried out using an impedance analyser 4192A in the frequency range of 100 Hz to 1 MHz with a probing voltage of 100 mV in the temperature range of 30°C–70°C.

**Results and discussion**

The GNPs were characterised by visible spectrophotometry; the respective spectra for NP1 and NP2 are displayed in Figure 1(b) and (c). NP1 because of the small size (1.77 nm) did not show a SPR peak while, the larger NP2 displayed the characteristic SPR. Size and size distribution of the nanoparticles were determined by transmissions electron microscopy (TEM) analysis. The TEM images for NP1 and NP2 are shown in Figure 2(a) and (b). All nanoparticles homogenously disperse in several organic solvents facilitated by the cholesterol-LC coating and showed no signs of agglomeration. The calculated sizes for NP1 and NP2 are 1.77 and 5.5 nm, respectively.

Polarised optical microscopy investigations reveal no change in the characteristic SmC* textures (not shown in the figures) and in either phase sequence or clearing point of the FLC at the expense of increasing GNP doping concentrations (0.1 and 0.5 wt.%). All nanocolloids homogenously disperse in several organic solvents facilitated by the cholesterol-LC coating and showed no signs of agglomeration. The invariance of phase sequence and textural morphology are taken as indicators for the dispersion of the GNPs in the FLC matrix.

As stated, NP1 and NP2 differ in the diameter of the gold NP core and the length of the flexible spacer (n = 6 and n = 11, respectively). Considering NP1 or NP2 as an entire ‘molecule’, the diameter of NP1 is approximately 7.4 nm and approximately 12 nm for NP2. The surface of the gold particles is around 9.83 nm² for NP1 and 96.4 nm² for NP2, which is nearly equivalent to the ratio of 45–450 ligands around the core, respectively. Following these rough estimations, 1.5 ‘molecules’ of NP1 are related to 10⁷ FLC molecules at 0.1 wt.% and for NP2 at 0.1%, the estimated ratio of NP2 to FLC is about 1.5 ‘molecules’ to 10⁶ FLC molecules. From these estimations with respect to the TEM images in Figure 2, one can conclude that there is no interaction between the nanoparticles, in other words, the key difference between both is at a first glance the difference in size.

Considering the effect of NP1 and NP2 on the physical parameters of the FLC-nano colloids, one of the most striking effect is the increase of the spontaneous polarisation from 180 nC/cm² at 30°C up to 212 nC/cm² for NP1 at 0.1% wt.% or even higher for NP2 (Figure 3(a)), definitely outside the error bar ±1 nC/cm². A similar trend was seen for the higher doping concentration (0.5 wt.%). For these nanoparticles, Hegmann et al. [15] described a chirality transfer via doping these chiral NPs into nematic LCs leading to chiral nematic LCs with negative CD Cotton effect. Our FLC mixture is chiral due to the 25% content of the chiral substituted S-terphenyl compound (see above), so the increase of spontaneous polarisation can be easily understood. Tuning of the spontaneous polarisation in FLCs through adding variable amount of chiral non-liquid crystalline samples is well known and practically used while preparing FLC mixtures with different spontaneous polarisation values.[17; Lapanik, V. personal communication] The minor difference in Ps for NP1 and NP2 is probably due to different amount of chiral groups surrounding the gold nuclei at NP1 and NP2, respectively.

The variation of primary order parameter tilt angle (θ) as a function of temperature for 0.1 wt.% and 0.5 wt.% GNP–FLC nanocolloids is presented in

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**Figure 2.** High-resolution TEM images of (a) NP1 (size: 1.77 ± 0.11 nm, scale bar: 10 nm) and (b) NP2 (size: 5.54 ± 1.23 nm, scale bar: 5 nm).
There is a general tendency of decrease in the tilt angle although singular data lie within the error bar of ±1°. Considering the small differences outside the error bar, the more significant decrease in tilt for NP2 at both concentrations (0.1 wt.% and 0.5 wt.%) could be attributed to the influence of the larger GNP core size and perhaps also the longer aliphatic chains of the functionalising ligands. The small variation in θ mainly for NP2 is in contrast to earlier reports on functionalised GNP–FLC and GNR–FLC nanocolloids. An increase in optical tilt for GNP–FLC nanocolloid was reported by Biradar and co-workers, and in their case, a localised electric field effect of the used bare, non-coated GNPs was considered for the cause. As to our own work on functionalised GNPs, we reported an unchanged tilt angle.

For the switching time (τ), a slight increase with increasing size of GNPs is seen as evident from the data presented in Figure 3(c). Comparing the two concentrations for NP1, the data are ordered within the error bar (±1 µs). By incorporating the GNPs, a slight increase in τ observed for the larger size GNPs is most likely a result of the increase in viscosity (see later).

In the present study, the changes of spontaneous polarisation and to a minor extent tilt angle and switching time were more pronounced comparing the GNP particles core size and functionalising ligands rather than their increasing concentration. A model for incorporating the GNPs for NP1 is shown in Figure 4.

Earlier studies revealed that GNPs in FLCs matrices produce a collective effect of electron wave plasmon oscillations in GNPs, and the electromagnetic wave from the photons of incident light interacting with the FLC molecules result in a plasmon polarisation effect. Such interaction between GNPs and FLC molecules would locally generate a slightly higher field in the sample and modulate the structural and electro-optic parameters of the nanocolloids.

In general, the external applied field $E_{\text{ext}}$ is modulated due to the ionic field $E_{\text{ion}}$ and the depolarisation field $E_{\text{dep}}$ leads to a change in the local electric field $E_{\text{loc}}$. Such modulation of $E_{\text{loc}}$ is also described for harvested BaTiO$_3$/FLC, LiNbO$_3$/FLC, fullerene/FLC, and CdSe QD/FLC nanocolloids. In these systems, however, the modulation of $E_{\text{loc}}$ is triggered by the capturing of impurity ions rather than plasmonic effects.

To analyse potential contributions of surface plasmonic effects in the present chiral ligand-capped GNP–FLC mixtures, $E_{\text{loc}}$ is calculated using Equation (1)
\[ \tau = \frac{\gamma_\phi}{F_s E_{\text{loc}}} \quad (1) \]

where \( E_{\text{loc}} \) is the local electric field and \( \gamma_\phi \) is the rotational viscosity (which has been calculated at first from dielectric data, see later). The calculated \( E_{\text{loc}} \) for the non-doped FLC and the two NP1 and NP2–FLC nanocolloids at 0.1 wt.% were 50.0, 52.1 and 51.7 V/\( \mu \)m, and at 0.5 wt.% 51.0 and 52.3 V/\( \mu \)m, respectively. Hence, on average, a small increase was observed. We also calculated the number of ions in the non-doped FLC and the two nanocolloids using the relation

\[ n_{\text{ions}} = \frac{d_{\text{LC}}}{ze\mu R_{\text{LC}} S} \quad (10) \]

where \( d_{\text{LC}} \) stands for cell thickness, \( z \) is the ionic charge, \( e \) symbolises the charge of the electron, \( \mu \) represents the ion mobility, \( R_{\text{LC}} \) and \( S \) stand for the resistance and area of the sample. \( n_{\text{ions}} \) calculated for the non-doped FLC and the NP1 and NP2 FLC nanocolloids were \( 1.5 \times 10^{21} \), \( 1.52 \times 10^{21} \) and \( 1.54 \times 10^{21} \) m\(^{-3}\)(at 0.1 wt.% GNP content) and for 0.5 wt.% concentration \( n_{\text{ions}} \) were \( 1.51 \times 10^{21} \) and \( 1.55 \times 10^{21} \) m\(^{-3}\), respectively. There is slight variation of \( n_{\text{ions}} \) after doping the FLC with the two GNP and their varying concentrations.

The slight increase in \( \tau \) at least for NP2 can also be understood on the basis of a rise in the rotational viscosity (presented and discussed later in this section) as Equation (1) reflects the direct proportionality amid the two quantities. The effect of longer aliphatic chains separating the cholesterol moiety interacting with the FLC host molecules and the GNP core may also slow down the response time of the nanocolloids. A comparison with data from previous reports on nanomaterial–FLC nanocolloids containing well-dispersed alkylthiol-capped GNP,[13] hydrophilic polymeercapped GNRs,[10] or LC-capped GNRs[14] highlights the critical role of ligand chirality and integration of the chiral ligand-capped GNP via a tactoidal ligand shell deformation.[25–26]

Finally, we also measured the complex dielectric permittivity (\( \varepsilon' \) and \( \varepsilon'' \)) for the FLC nanocolloids and compared the values to the non-doped FLC (Figure 5(a) and (b)). A remarkable increase for the loss factor maxima was observed after GNP doping, which obviously stems from introduced ions. The experiment data is best fitted with the standard Cole–Cole equation (Equation (2)) [22–24]

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha} \quad (2) \]

The Goldstone mode strength \( \Delta \varepsilon \) for the non-doped FLC and the nanocolloids is estimated from the Cole–Cole plot viz. \( \Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty \). The obtained magnitude of \( \Delta \varepsilon \) for the non-doped FLC as well as the NP1 and NP2–FLC nanocolloids as a function of temperature is plotted in Figure 5(c) demonstrating an increase of delta epsilon for the doped systems.

As the impact of increasing doping concentration is prominent on the dielectric properties (\( \varepsilon' \), \( \varepsilon'' \) and \( \Delta \varepsilon \)) of nanocolloids, we calculated the relaxation frequency and the rotational viscosity for the higher concentration nanocolloids 0.5 wt.% for NP1 and NP2.

![Figure 4.](https://example.com/figure4.png)

Figure 4. (Colour online) Models of the integration of chiral ligand-capped GNPs into the layer structure of an FLC host in planar cells (cell gap of a few micron). The model assumes a tactoidal deformation of the ligand shell facilitated by aliphatic spacers between the chiral ligands and the GNP surface. Little layer buckling is induced by the smaller GNP NP1.
A plot of $\log_{10} (v/u)$ versus $\log_{10} f$ gives a straight line, where the intercept on the abscissa corresponds to the relaxation frequency (plots are shown in Figure S1, Supplemental data). The calculated values of $f_G$ for the non-doped FLC and the GNP–FLC nanocolloids as a function of temperature are shown in Figure 6(a) for 0.5 wt.% concentration of NP1 and NP2. At 30°C, a substantial decrease in $f_G$ is observed for the GNP-doped FLC mixtures. $f_G$ increases with temperature for all systems and saturates around 45°C. A further rise in temperature reduces $f_G$.

Considering the dielectric and electro-optic parameters of the Goldstone mode, the rotational viscosity $\gamma_G$ was calculated using Equation (5) [22–24]:

$$\gamma_G = \frac{1}{4\pi\varepsilon_0\Delta\varepsilon_G f_G} \left(\frac{P_s}{\theta}\right)^2$$

Figure 5. (Colour online) Frequency dependence of (a) the dielectric permittivity, (b) the absorption strength and (c) dielectric permittivity for non-doped FLC and FLC nanocolloids of 0.1 and 0.5 wt.% GNP concentration at 30°C.

Figure 6. (Colour online) Temperature dependence of (a) the Goldstone-mode frequency $f_G$ and (b) the rotational viscosity $\gamma_G$ calculated from the dielectric parameters of the non-doped FLC and FLC nanocolloids of 0.5 wt.% GNP concentration.
The variation of γG as a function of temperature for the non-doped FLC and the NP-doped FLC (0.5 wt.% for NP1 and NP2) mixtures is presented in Figure 6(b). Marginal increase in γG (± 0.1 PaS) is seen for the NP1-doped nanocolloids, while it is prominent for the NP2.

An enhancement of both the dielectric constant and the dielectric strength in the FLC nanocolloids may be due to the ions. The ac conductivity for the non-doped FLC and the two FLC nanocolloids was calculated via the relation σac = εω|ω|. Further, σac as function of frequency could be written as σac = σdc + Aωγ6,[27] where σdc is dc conductivity and both A and n are fitting parameters. σdc could be estimated by fitting σac as function of frequency. The obtained conductivity values were 5.1 × 10⁻⁷ Sm⁻¹, 2.1 × 10⁻⁶ Sm⁻¹ and 3.6 × 10⁻⁶ Sm⁻¹ for the non-doped FLC and the two FLC nanocolloids doped with NP1 and NP2 at 0.5 wt.%, respectively. Interestingly, doping the FLC with the GNPs increases the conductivity by about to 1 order of magnitude, which could also contribute to the observed increase of the dielectric parameters up to some extent via introducing of ions.

The decrease in fG after GNP doping can be understood via the relation fG = Kq²/2pyG, where K is the Frank elastic constant, and q is the wave vector of the helix. fG and γG follow an inverse relationship. The increase in γG could be responsible for the decrease in fG observed for the FLC nanocolloids in comparison to the non-doped FLC.

Conclusion

GNPs capped with chiral, cholesterol-thiolate are used as additives in an FLC mixture. To determine the importance and role of these GNP parameters, i.e. size, number of chiral ligands and chiral bias, we measured the electro-optic and dielectric response of the resulting FLC nanocolloids. The phase sequence and phase transition temperatures are not affected by the GNP additives and their varying concentrations, although for the mixtures containing the larger GNPs NP2 a small change in the order parameter and in the switching time may be attributed to the larger NP size. The remarkable increase in the spontaneous polarisation with addition of chiral dopant GNPs to the chiral FLC matrix can be highlighted as a most significant result of the studied FLC nanocolloids. This is in contrast to some of our former experiments on FLC–GNP nanocolloids using non-chiral-surrounding ligand shell leading to decrease in spontaneous polarisation.

Our data show evidence for plasmonic effects to a minor extent and only marginal modulation of Eloc or change in nions upon doping the FLC with the GNPs. Larger GNP featuring the highest number of chiral dopant molecules in the ligand shell most likely induces the greatest hindrance of motion for the surrounding FLC host molecules. This effect overwrites potential contributions of the GNP core or surface chirality from the two GNPs, NP1 and NP2, which are synthesised in the presence of a chiral bias. An increase in both dc conductivity and the Goldstone mode viscosity are likely responsible for the decrease in the relaxation frequency for the FLC nanocolloids.

Disclosure statement

No potential conflict of interest was reported by the authors.

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