SYNTHESIS AND CHARACTERIZATION OF CITRATE CAPPED GOLD NANOPARTICLES AND THEIR EFFECT ON LIQUID CRYSTALS: OPTICAL STUDIES

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ABSTRACT

In the present paper synthesis and characterization are carried on citrate capped Gold (Au) nanoparticles dispersed in Liquid Crystalline p-n-Hexyloxycyanobiphenyl (6OCB) compound. We have reported citrate capped Au nanoparticles are synthesized by chemical reduction method which is having a broad range of applications and dramatically effects the birefringence properties of 6OCB when dispersion with low concentration. The Polarizing Microscopy (POM) technique is used to measure the phase transition temperatures. Further characterization is carried out by various spectroscopic techniques like X-ray Diffraction Studies (XRD), Scanning Electron Microscopic studies (SEM), Ultra Violet Visible (UV) spectroscopy. Textural determinations of the synthesized compounds are recorded by using POM connected with a hot stage and camera. The results showed that the dispersion of citrate capped Au and in 6OCB exhibit nematic phase as same as the pure 6OCB with slightly reduced clearing temperature as expected. Further, the birefringence anisotropy of 6OCB with dispersed citrate capped Au nanoparticles increases by 14%. It is found that the birefringence anisotropy as well as orientation order parameter of 6OCB increases with dispersed citrate capped Au nanoparticles.

Keywords: Synthesis, POM, DSC, Nano-dispersion, XRD, SEM, UV and Birefringence.

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INTRODUCTION

Liquid crystals (LCs) are mesophases with a degree of order in between that of solid and liquid exhibiting anisotropic properties. LCs are self-assembled dynamic functional soft materials which possess both order and mobility at molecular, supra molecular and microscopic levels¹-³. The anisotropy properties include birefringence, viscosity, elasticity, dielectric permittivity etc. The flow property allows them to be contained in any container. These two properties make these LC materials as viable candidates for applications. The display technology needs the knowledge of the LC behaviour in electric field and optical properties⁴.LCs not only having in applications in displays⁵,⁶ and is also a useful medium for nonlinear optics⁷. For examples, laser induced thermal⁸,⁹ and orientational¹⁰,¹¹ effects in dye-doped LC are fundamentally interesting and practically useful phenomena. If LC exhibits a large temperature-gradient refractive index, then the required laser intensity for triggering the nonlinear optical effects to occur is reduced.

A variety of applications has been takes place while dispersion of metal nanoparticles in to the moiety of LC. These nano doping materials investigated include metallic nanoparticles, semiconducting nanoparticles, ferroelectric nanoparticles, carbon related nanoparticles and other. Recently, metal nano clusters, particularly gold nanoparticles, have attracted a great deal of interest since they show unusual properties compared to bulk metals. Gold nanoparticles are the most stable metal nanoparticles and they
present fascinating aspects such as, their self-assembly, the behaviour of individual particles, size related electronic, magnetic and optical properties and their applications as catalysis. The synthesis of monolayer-protected gold nanoparticles in organic solvents by Brust and co-workers has opened a whole new field in material science. Since the properties of metal nanoclusters aggregates are affected by their morphology, various attempts to control their morphology have been performed by means of physical and chemical processes.

The orientational order parameter $S$ is one of the most important material parameters of the nematic phase, which determines all of its anisotropic properties and the relations between macroscopic and microscopic properties. Different techniques are employed for the determination of birefringence due to its importance. The order parameter can be measured experimentally in a number of ways, for instance, diamagnetism, birefringence, Raman Scattering, NMR and EPR can be used to determine $S$. Most of the research workers are calculating order parameter using birefringence by the method used by Kuczynski et al. The advantage in this method is that no field is assumed to describe the nematic phases and the order parameter can be calculated in smectic phases also provided the refractive index is obtained experimentally in the smectic phases. Rao et al. have published their results on different oxide materials, luminescent materials and polymers in their earlier studies. In the present paper Au nanoparticles are capped with citrate and dispersed in p-n-Hexyloxy cyanobiphenyl (6OCB) and characterized by various experimental techniques namely UV, SEM, XRD and Modified Spectrometer.

**EXPERIMENTAL**

*Synthesis of Citrate capped Ag nanoparticles*

LC compound such as 6OCB, Auric Chloride (HAuCl$_4$) and trisodium citrate dehydrate (Na$_3$C$_6$H$_5$O$_7$•2H$_2$O) 99% are brought from Sigma-Aldrich laboratories, USA and used as such. Citrate capped Au nanoparticles are synthesized in the laboratory from the citrate reduction process. First, 20 ml of 1mM of Auric Chloride is heated and 2ml of 1% trisodium citrate is added drop by drop and stirred vigorously for two hours. Then the solution changed gradually to red wine color indicates the formation of citrate (ct) capped Au nanoparticles. The ct capped Au nanoparticles synthesized by this manner as citrate served the dual purpose of being the reducing agent as well as stabilizer.

*Dispersion of citrate capped Au nanoparticles in LC compounds*

For uniform dispersion of nanoparticles in LCs, the nanoparticles are first dissolved in toluene, stirred well about 45 minutes and later introduced in the isotropic state of mesogenic material (6OCB) in quantity 30 µl and 50 µl separately and the complex mixture is stirred about 3 to 4 hours. After cooling, the nanocomposite6OCB is subjected to study of the textural and phase transition temperatures using a polarizing optical microscope (SDTECHS make) with a hot stage in which the substance was filled in planar arrangement in 4 µm cells and these could be placed along with the thermometer. Textural and phase transition temperatures are studied after preparation of the sample and observations are made again to understand the stability of nanoparticles. The presence of ct capped Au nanoparticles in 6OCB is studied by UV and SEM data and existence as well as size is determined by XRD technique.

**RESULTS AND DISCUSSION**

*Polarizing Optical Microscope*

The LC molecule is characterized by different LC phases due to the change in the local molecular order with the temperature giving rise to different phases. Determination and characterization of these mesophases will provide very important information on the pattern and textures of the LCs. The transition temperatures and textures observed by Polarizing Microscope in 6OCB with dispersed ct capped Au nanoparticles with concentration 30 µl shown in Fig.1 (a-c) and that of concentration 50 µl shown in Fig.-2 (a-c) respectively. The thermal ranges of nematic phase are changed slightly due to the dispersion of nanoparticles and the textures of the nematic phase are changed by the self-assembly of nanoparticles.
Textures of 6OCB with 30µl citrate capped nanoparticles

(a): nematic at 72.6 °C
(b): Stabilized Nematic Phase at 71.1 °C
(c): Solid at 47.5 °C

Textures of 6OCB with 50µl citrate capped Au nanoparticles

(a): Isotropic to nematic at 72.7 °C
(b): Schliren nematic at 48.2 °C
(c): Nematic-Solid at 64.3 °C

Ultraviolet –Visible Spectroscopy

Fig.3 shows the UV-visible spectra of pure and 30 µl ct capped Au nanoparticles dispersed in 6OCBLC sample. It is observed that the spectrum for pure 6OCB does not exhibit any absorption peaks in the wavelength range 500–600 nm. However, the spectrum of nanodoped 6OCB shows the significant peak at 545nm, which is the characteristic peak of ct capped Au nanoparticles. So, the UV-visible spectral study confirms the presence of ct capped Au nanoparticles in the prepared nanodoped LC. The decrease in the absorbance in nanocomposite 6OCB resembles that the capping of the 6OCB LC molecules with the nanoparticles.

SEM analysis

The SEM provides the investigator with a highly magnified image of the surface of a material as the present sample contains electrons; which are needed for getting SEM image. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from about 10X-
300,000X. SEM gives not only topographical information but also gives the information regarding the composition of the elements in the material\textsuperscript{31}. The SEM images of ct capped Au nanoparticles and with the dispersion of 30 µl ct capped Au nanoparticle in 6OCB is shown in the Fig.-5 and Fig.-7. It is clear from Fig.-5 that the nanoparticles are in the size of approximately 29 nm. The EDS data elucidates the presence of nanoparticles in the compound is well established.

![UV-visible spectra of 6OCB with dispersed 30 µl ct capped Au nanoparticles](image1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>66.75</td>
<td>73.42</td>
</tr>
<tr>
<td>O</td>
<td>32.09</td>
<td>26.50</td>
</tr>
<tr>
<td>Au</td>
<td>1.17</td>
<td>0.08</td>
</tr>
</tbody>
</table>

![EDS data of citrate capped Au nanoparticles](image2)

![SEM Image](image3)
XRD Analysis
The XRD data of 6OCB with dispersed 50 µl of ct capped Au nanoparticles are shown in Fig.-8 and Fig.-9 respectively. In comparison of JCPDF data peaks were well resolved and are matched with JCPDF card no. 03-065-2870 which is clearly evidenced the existence ct capped Au nanoparticles. By using Scherrer’s Formula, $t = \frac{k\lambda}{\beta\cos\theta}$, the grain size is found to be 29 nm, $\Lambda=1.54$ Å, $\beta=\text{FWHM}$, Peaks at 38.218°, 44.296°, 64.487° and 77.467° resembles the existence of ct capped Au nanoparticles.
Estimation of Orientational Order parameter S from Refractive Indices data

(a) Optical Birefringence Studies

The refractive indices of 6OCB pure and 6OCB with 50 µl ct capped Au nanoparticles dispersion are measured using the modified spectrometer and a wedge shaped cell with temperature accuracy ± 0.1 °C. The refractive indices $n_e$ and $n_o$ are measured at wavelength 589.3 nm. The refractive index in the isotropic phase shows very nominal increment with the decrease of the temperature.

![Fig.-9: Refractive index of 6OCB pure](image1.png)

![Fig.-10: Refractive index of 6OCB + 50 µl ct capped Au](image2.png)

![Fig.-11: Variation of $\delta n$ with temperature in 6OCB Pure 6OCB + 50 µl ct capped Au nanoparticle dispersion](image3.png)
At the I-N phase transition, the isotropic value splits into two, one value higher and another lower than isotropic value corresponding to extra-ordinary ($n_e$) and ordinary ($n_o$) refractive indices respectively. This is clearly observed in the telescope of modified spectrometer at the angle of minimum deviation. In the nematic region, $n_e$ increases while $n_o$ decreases with the decrease of temperature. Fig. 9 and Fig.10 represents the variation of refractive indices in 6OCB and 6OCB with 50 µl ct capped Au nanoparticles. It is found that I-N transition temperature decreased with nanoparticles dispersion which is shown in the DSC and POM values. Further, the birefringence values obtained for 6OCB is nearly equal with the previously published data. Birefringence property and its dependency on molecular reorientation play an important role in understanding the molecular reorientation mechanisms\(^3\). It is further found that the birefringence anisotropy, $\delta n = n_e - n_o$ values with respect to temperature increases by 14 % with the dispersion of ct capped Au nanoparticles as shown in the Fig.11. It resembles the self-alignment of nanoparticles with 6OCB molecules and thereby the view angle increases which will be very much useful in display devices.

**(b) Estimation of order parameter S from Birefringence $\delta n$**

Kuczynski et al.\(^{1b}\) proposed a simple procedure for the determination order parameter S from the birefringence measurements $\delta n$ without considering the local field experienced by the molecule in a liquid crystal phase. The birefringence $\delta n$, which is a function of temperature is fitted to the following equation, $\delta n = \Delta n \cdot (1 - (T/T^*))^\beta$. Where T is the absolute temperature, $T^*$ and $\beta$ are constants. ($T^*$ is about 1-4 K higher than the clearing temperature and the exponent $\beta$ is close to 0.2). This procedure enables one to extrapolate $\delta n$ to the absolute zero temperature. In practice, the three adjustable parameters $T^*$, $\Delta n$ and $\beta$ were obtained by fitting the experimental data for $\delta n$ to the following equation written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta \log \left\{1 - \frac{T}{T^*}\right\}$$

In the present investigations, the value of log $\Delta n$ and $\beta$ are estimated by the linear regression and the corresponding values for 6OCB and 6OCB + 50 µl ct capped Au nanoparticles dispersion is shown in the Table 1. Log-log plots of 6OCB and 6OCB + 50 µl ct capped Au nanoparticle dispersion is shown in Fig.12. Only the nematic range is considered for the evaluation of $\Delta n$ from this method. The order parameter $S$ value is estimated from the equation $S = n_e - n_o$. Where $\Delta n$ is the birefringence anisotropy in perfect order which is obtained from the log-log plots of experimental $\delta n$ and the reduced temperature and the particulars are described in reference\(^3\). The variation of order parameter LC compound pure 6OCB and 6OCB + 50 µl ct capped Au nanoparticles dispersion with temperature is shown in Fig.13. While dispersing the Au nanoparticles in 6OCB, the order parameter is increased by 6.5%. The order parameter enhancement is of primary importance for the innovation of different electro-optic applications.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T^<em>$ =~$T^</em>$</th>
<th>Slope ($\beta$)</th>
<th>Log($\Delta n$)</th>
<th>$\Delta n$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>6OCB pure</td>
<td>2.9</td>
<td>0.2198</td>
<td>-0.4384</td>
<td>0.367</td>
<td>0.9959</td>
</tr>
<tr>
<td>6OCB + 50µl ct capped Au nps</td>
<td>0.1</td>
<td>0.1879</td>
<td>-0.3991</td>
<td>0.399</td>
<td>0.9991</td>
</tr>
</tbody>
</table>

**CONCLUSION**

With the present results we demonstrated the dispersion of ct capped Au nanoparticles in LC 6OCB changing of their textures, phase transition temperatures and shifts in vibrational bands by using Polarizing Microscope and Fourier Transform Infra Red techniques respectively. The presence of ct capped Au nanoparticles in LC 6OCB is also confirmed by the EDS data of SEM and UV spectrometry.
X-Ray diffraction confirms that no alteration of its structure and also the existence of the ct capped Au nanoparticles. It is further found that the birefringence anisotropy, $\delta n = n_e - n_o$ values with respect to temperature is increased by 14% with the dispersion of ct capped Au nanoparticles and the order parameter $S$ is increased by 6.5%.

Fig.-12: The log–log plot of $\delta n$ versus reduced temperature for compound 6OCB pure and 6OCB with 50µl ct capped Au nanoparticles

Fig.-13: Order parameter, $S$ versus temperature for the compound 6OCB pure and 6OCB with 50 µl ct capped Au nanoparticles

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