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Cholesterol Phenoxy Hexanoate Mesogens: Effect of *meta* Substituents on Their Liquid Crystalline Behavior and in Situ Metal Nanoparticle Synthesis

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Designing small molecules which self-assemble to generate nanoscale materials is an exciting area of current research interest.[1] Within this field, the self-organized systems of liquid crystals (LCs) are well-studied in the literature.[2−4] In particular, lateral substitution of LCs affects the mode of assembly and subsequently properties of self-assembled materials.[5,6] It is known that the length of the flexible chain as well as suitably attached functional groups on the rigid core of the mesogens influences the LC properties and their melting temperatures. Appropriate substitution in a mesogen leads to an increase in its breadth and reduces the length to breadth ratio. According to the van der Waals molecular static theories the *meta* substituents usually decrease the melting temperature.[6]

Recent studies indicated that in situ synthesis of metal nanoparticles (MNPs) within the self-assembled architectures is a feasible and convenient approach to generate MNPs embedded soft materials.[7,8] LC templated synthesis of nanostructured materials and nanoparticles (NPs) have been reported in the literature.[1,3,8,9] Incorporation of metal NPs in LCs produces material that possesses properties of metal particles and that of soft matter.[9−12] Attempts have also been made to incorporate various MNPs in LCs to improve the optical properties of LCs.[2,3,9b,11,13] Currently, NPs embedded LCs were prepared by external doping of NPs into LCs; similarly, NPs have been doped in molecular gels as well.[14] However, most of these processes are multistep, which involve separate synthesis of MNPs, their functionalization, and doping of particles in LC domains. Hence, we propose developing LCs with suitable functional groups, which can act as reducing agents for metal salts to genarate MNPs within the LC phases in a single step. In our earlier study, monosubstituted urea and ascorbic acid have been used to develop amphiphilic gelators and mesogens to synthesize, stabilize, and align gold nanoparticles (GNPs) within the nanoaggregates.[7,8]

In continuation of previous work, we designed a series of cholesteryl phenoxy alkanoates (CPAs) as versatile mesogens

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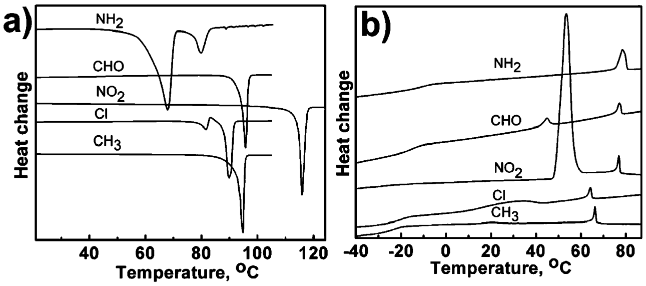
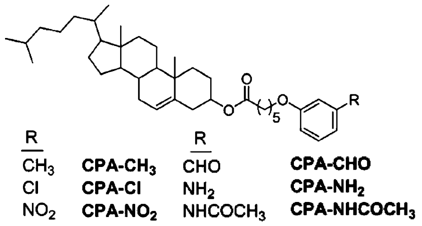


Figure 1. DSC thermograms for (a) heating and (b) cooling cycles.

Scheme 1. Chemical Structures of Mesogens



(Scheme 1). The interest behind the design of mesogens consisting of a cholesteryl group arises from its long rigid shape, chiral nature, and tendency to form glassy phases, which preserve the optical properties of LCs in the solid state.[15] Existing glassy LCs are characterized as twin molecules or unsymmetrical dimesogenic systems.[16] However, how the presence of different *meta* substituents on CPAs affect their inherent LC properties is a topic worth study. Systematic design includes selecting appropriate functional groups to alter the dipolar moments and introducing moderate and extended hydrogen bond forming ability. Aldehyde[17] and aromatic amine[18,19] functional groups are known to reduce gold salts to make GNPs. Hence, can mesogens with CHO and NH_2 groups reduce metal salts to generate MNPs by in situ synthesis? To answer this intriguing question, we have designed and studied the influence of various substituted functional groups such as CH_3, Cl, NO_2, CHO, NH_2, and $NHCOCH_3$ on the *meta*-position of the phenyl ring (Scheme 1).

The effect of linker alkyl chain length on CPAs has been reported in the literature,[20] but surprisingly, the effect of *meta*-substitution on the phenyl group has not been documented (especially with terminal amine and aldehyde functional groups which can reduce the metal salts to generate NPs). Hence, we explored these properties in the present investigation. We also report the in situ synthesis of GNPs and platinum nanoparticles (PtNPs) and their stabilization using the above-mentioned mesogens. Detailed synthetic procedures and characterization of mesogens are given in Supporting Information.

Study of Liquid Crystalline Properties. LC properties of mesogens were studied using optical polarizing microscopy (OPM) and the phase transition temperatures, which were confirmed using differential scanning calorimetry (DSC). Thermal properties of LCs are summarized in Table S1 (Supporting Information). Table S1 evidences that except for CPA-$NHCOCH_3$ all other derivatives exhibited thermotropic liquid crystalline properties during cooling cycle. Interestingly, only CPA-NH_2 showed an enantiotropic LC phase during the heating cycle. Mesogen with a methyl group (CPA-CH_3) exhibited a monotropic meso phase at 66.2 °C in the cooling cycle. Both the fingerprint texture and the single color reflecting Grandjean texture[21] exhibited in this compound confirms the formation of a N* (chiral nematic) phase (Supporting Information). Upon further cooling slowly, CPA-CH_3 crystallized at 23.8 °C. Similarly CPA-Cl also exhibited a monotropic N* phase from 64.2 °C to 41.8 °C (Supporting Information).

DSC thermograms in the cooling cycle of CPA-CH_3 and CPA-Cl did not show a clear exothermic peak for the N*−Cr transition, which could be due to the slow crystallization process (Figure 1a,b). We also reasoned that the small difference in melting temperatures upon changing the substituent from CH_3 to Cl could be due to their similar length to breadth ratio, which is supported by the previous studies on similar systems.[6] The mesogen CPA-NO_2 having a nitro group on the *meta* position of the phenyl ring also exhibited a monotropic N* LC phase from 76.9 °C to 53.4 °C. The foremost difference observed in case of CPA-NO_2 compared to that of CPA-CH_3 and CPA-Cl is higher transition temperature from the Iso-N* to the N*-Cr phase. The observed slightly elevated temperature for CPA-NO_2 could be explained using the polarity effect of the nitro group. It has been shown in an earlier report that high polar compounds have much higher packing density. Hence, the increase in packing density accounts for the increasing clearing temperatures in CPA-NO_2.[6] In CPA-CHO the monotropic N* phase was observed from 77.2 °C to 45 °C which upon cooling transformed to SmA* (chiral smectic A) phase (for OPM image see Supporting Information). The SmA* phase was identified from the characteristic focal conic textures with homeotropic regions.[21] We speculate that the formation of a more ordered mesophase in CPA-CHO at lower temperature could be due to the dipolar moment of mesogen; however, in addition, hydrogen bonding interactions of the CHO groups also may play a role in determining the LC phase along with the dipolar moments. At lower temperature, intermolecular hydrogen bonding interactions of the CHO groups may encourage the lateral interactions lining up the molecules in a layered arrangement (see Supporting Information).[22]

In this series, CPA-NH_2 exhibited an enantiotropic LC phase. Upon heating, CPA-NH_2 showed a SmA* phase from 67.9 °C to 79.8 °C (for OPM images see Supporting Information). Intriguingly, during heating cycles, among all

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the mesogens studied only CPA-NH_2 exhibited an enantiotropic LC phase. The formation of a smectic phase of CPA-NH_2 was also expected to be similar to CPA-CHO LC formation, where hydrogen bonding influences the mode of self-assembly. In the case of CPA-NH_2, primary amine groups increase the intermolecular interactions.[22] To study the effect of hydrogen bonding interaction on the LC properties, we have synthesized CPA-$NHCOCH_3$ having an acetanilide group on the *meta* position of phenyl ring. CPA-$NHCOCH_3$ did not show any LC phase during heating or cooling cycles. Acetanilide is known to form extended H-bonding networks compared to amine or aldehyde. Previously Gray proposed that strong intermolecular hydrogen bonding raises the melting point above the mesophase–isotropic liquid transition temperature.[23] Similarly we believe this because strong intermolecular hydrogen bonding in CPA-$NHCOCH_3$ caused the absence of mesophase formation and there is a higher melting point in this present series of compounds. Hence, CPA-$NHCOCH_3$ crystallized without showing any liquid crystalline property.

In Situ Synthesis and Characterization of NPs. Systematic study on LC properties of mesogens prompted us to investigate the possibility for in situ synthesis of MNPs within the LC phases. Earlier, we successfully demonstrated the preparation of novel organic–inorganic hybrid nanomaterials using self-assembled hydro/organo gels[7] and LCs[8] as media for in situ synthesis of GNPs.

In continuation to our previous efforts, present interest is to generalize the concept of soft material mediated NP synthesis and to perform in situ synthesis of MNPs in LCs using a reducing functional group containing mesogens. In the present study we took advantage of reducing abilities of aldehyde[17] and aromatic amine[18,19] functional groups to genarate MNPs. The aldehyde/amine group which is a part of the mesogen will serve as a reducing agent for converting Au(III) to Au(0), and in the process GNPs would be generated in LC phases.

GNPs containing LC films were prepared as follows. Mesogen CPA-CHO was dissolved in acetone (2 mL), to which $HAuCl_4$ (5 mol %) in acetone was added, and the solution was drop-casted on a glass plate. The film which was obtained after solvent evoporation was heated at 120 °C (isotropic phase) for 10 min and slowly cooled to room temperature. Upon heating there were visually observable changes in the film. First, yellow color of the film rapidly changed to colorless and then to a pale pink hue (see Supporting Information). The absorption spectrum of the film was taken at 25 °C, and it showed a characteristic plasmon resonance band of GNPs at $\lambda_{max} = 562$ nm. GNPs encapsulated (prepared using 5 mol % $HAuCl_4$) also showed monotropic LC properties similar to the parent compound CPA-CHO. Upon cooling CPA-CHO, the N* phase was observed at 54.2 °C, which transformed to the SmA* phase at 41.7 °C (for OPM image see Supporting Information). Following a similar procedure, GNPs were prepared using CPA-NH_2, and examination of LC properties of GNPs with the embedded CPA-NH_2 LC (CPA-NH_2:GNPs) system exhibited properties indentical to those of the parent CPA-NH_2 LC system. This indeed suggested that in situ synthesized GNPs were stabilized within the LCs without altering inherent LC behavior of unmodified mesogens. To probe the effect of $HAuCl_4$ concentration we carried out experiments with different concentrations; at higher amounts (~20 mol %), we observed the phase separation, and the best results were obtained with 5 mol % concentration, which was used for further experiments. To explore the thermal behavior of LC-GNP conjugates we carried out DSC experiments, and interestingly, an increase of about 11 °C in the LC-glass transition temperature was observed in CPA-NH_2:GNPs prepared using 5 mol % of $HAuCl_4$, compared to CPA-NH_2. It is known that the physical mixture of LC-NP hybrid systems lowered the phase transition temperatures because of the chemisorption of mesogens on NPs.[2b,4] However, in the present system GNPs were generated in situ using mesogens as reducing and stabilizing agents. Hence, it is expected that there would be no further chemisorption after NPs were capped with mesogens, which stabilizes the LC phases.

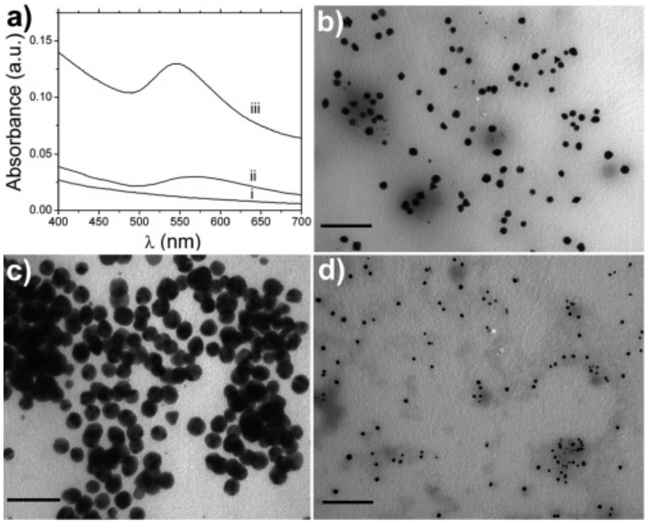

Figure 2. (a) Absorption spectra of (i) only CPA-NH_2 in solution and GNPs prepared by (ii) CPA-CHO and (iii) CPA-NH_2. TEM images of GNPs prepared by (b) CPA-NH_2 and (c) CPA-CHO and (d) PtNPs prepared by CPA-CHO. Scale bars represent 100 nm.

In situ prepared GNPs were characterized by UV–visible spectroscopy and transmission electron microscopy (TEM). Typically, GNP embedded film was dissolved in acetone and subjected to absorption experiments. Strong absorption peaks at longer wavelengths correspond to the surface plasmon band of GNPs suggesting the presence of particles in nanoscale dimensions. The observed λ_{max} values for GNPs synthesized with reductants CPA-NH_2 and CPA-CHO were 548 and 562 nm, respectively (Figure 2a). For TEM analysis a drop of GNPs containing acetone solution was placed on a TEM grid and dried in vacuo. Careful analysis of TEM showed the presence of well-dispersed GNPs, which were mostly spherical in shape. The GNPs synthesized in the CPA-NH_2 LC system were uniformly distributed with average size of 12–16 nm. While mostly spherical shaped particles were present, and occasionally triangular, square, and diamond shaped NPs also were observed (Figure 2b). In comparison,

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GNPs prepared in the CPA-CHO LC system are larger in size with an average diameter of 14−20 nm and a spherical in shape (Figure 2c, particles sizes were obtained from histogram analysis, for images see Supporting Information). To test the application of this approach for other metals, the reduction process was carried out with chloroplatinic acid to generate PtNPs. Mesogen CPA-CHO generated PtNPs were well dispersed and small in size, 4−6 nm (Figure 2d).

The literature survey showed that amine and aldehyde groups can reduce the metal salts to generate NPs;[17−19] hence, we hypothesized that the terminal amine/aldehyde group of mesogens are acting as reducing agents, subsequently binding to Au(0) and Pt(0) to stabilize them. To shed light into this hypothesis, we carried out a similar reduction process with CPA-$NHCOCH_3$, which resembles the structure of CPA-NH_2 except for the terminal acetanilide group; thus, lack of terminal amine group should prevent the gold reduction process. As anticipated, CPA-$NHCOCH_3$ failed to reduce the metal salts under similar conditions to produce the NPs. These results unambiguously proved that modulation of reduction properties of mesogens can be achieved by choosing the appropriate functional group.

In conclusion, we synthesized a series of *meta* substituted mesogens of CPAs containing various end functional groups and systematically studied their effect on LC properties. In situ synthesis of MNPs has been achieved with these mesogens without using any external reducing and stabilizing agents. The inclusion of GNPs in LCs did not change the inherent LC properties while LC phases were thermally stabilized. In situ synthesized LC-MNPs were fully characterized, and hybrid materials were stable for several months. The preparation of organic−inorganic hybrid materials with high order nano- or micro-structures would have applications in developing materials with tunable optical, electrical, and catalytic properties. The possibility of aligning the MNPs into desired arrays using LCs as templates is currently under investigation.

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Supporting Information Available: Materials and methods, OPM images, synthesis, and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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