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Enhancement in the thermodynamic, electrical and optical properties of hexabutoxytriphenylene due to copper nanoparticles

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ABSTRACT

In the present article, we have studied the effect of copper nano-particles on the thermal, optical and dielectric parameters of a liquid crystalline material 2,3,6,7,10,11-hexabutyloxytriphenylene (in short HAT4) showing wide temperature range (~65 °C) hexatic columnar mesophase. A composite has been prepared by dispersing 0.6 wt.% of copper nano-particles. UV–vis spectroscopy has been used to record the absorption spectra. It has been observed that the presence of copper nano-particles introduces surface plasmon resonance and reduces the optical band gap of HAT4. Though isotropic to mesophase transition temperature is unaffected but mesophase-crystal transition temperature has decreased and hence range of the mesophase has enhanced due to the presence of copper nano-particles. While dc conductivity has increased by about two orders of magnitudes, dielectric permittivity has also moderately increased. With the enhanced properties, HAT4-copper nano-particle composite is useful for one dimensional conduction and photovoltaic applications.

1. Introduction

Discotic liquid crystals (DLCs) are nanomaterials with disc diameter 2–6 nm. DLCs are appropriate materials for one-dimensional organic semi-conduction [1]. Further, due to electron and hole conduction, DLCs have been suitable material for electronic and opto-electronic devices, such as organic photo voltaic solar cells, organic light emitting diodes, field effect transistors, one-dimensional conductors, photo conductors and gas sensors [1–6]. DLCs were discovered in 1977 by Chandrasekhar et al. [7,8]. Composed of disc shaped molecules [9], DLCs are robust materials because of their one-dimensional charge conduction, long range mesophase and self-organizing columnar structure. Its molecule consists of rigid aromatic core, which is surrounded by flexible peripheral substituents and aromatic cores self stack one on top of other to form a columns [1,10]. Such mesophase of DLCs is known as columnar phase.

Due to the short stacking gap (~0.35 nm) relative to inter-columnar (two adjacent columns gap i.e. 2–6 nm, depending on length of lateral chains), the movement of generated charges in DLC from one molecules to other molecules is in the stacking direction and columns in DLCs are treated as molecular conducting wires with surrounded insulating aliphatic chains [1,11]. The disc molecules in DLCs are aligned in two directions; one is columns parallel to the substrates (planar alignment) and other is columns perpendicular to the electrode coated substrates (homeotropic alignment) [12,13]. Both types of orientations of molecules can be used in different applications. Parallel alignment is useful for field effect transistor while homeotropic alignment is useful for photovoltaic solar cells and light emitting diodes [13–17]. These alignments of molecules can be achieved by slow cooling of DLC materials from their isotropic liquid phase to room temperature, after filling in the dielectric cells [18].

The present work, focused on dielectric, optic and thermal properties of triphenylene based DLC material (i.e. 2,3,6,7,10,11-hexabutyloxytriphenylene (HAT4)) and its composite with copper nanoparticles. In triphenylene compound, three benzene rings fuse to form common fourth ring and its electron rich nature is suitable for doping with electron acceptor [2,19]. Its short chain length may decrease the degree of disorder in packing of the molecules within the column and also shows relatively high value of parallel and perpendicular component of conductivity [10,20,21]. The Cu nanoparticles have been dispersed to tune the properties of pure HAT4 from application point of view. Due to the existence of a localized surface plasmon resonance (SPR) and enhancement of light harvesting properties of metal (i.e. Au, Ag & Cu) nano-particles (NPs), we have concerned on Cu NPs, because of their unusual optical, electronic and chemical properties which depend on their size, shape, composition, crystallinity structure and dielectric environment around the nano-particles [22–24]. In the present work, low percentage (0.6 wt.%) of Cu nano-additives has been used to reduce the problem of immiscibility and aggregation. The molecular structure of the investigated DLC compound HAT4 is shown in Fig. 1. HAT4 shows hexatic plastic columnar phase (Col_{hp})

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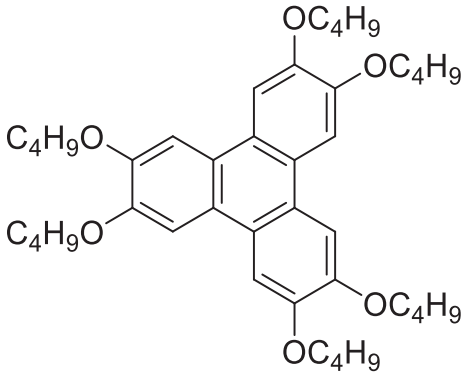

Fig. 1. Molecular structure of 2,3,6,7,10,11-hexabutoxytriphenylene (HAT4).

between its crystal and isotropic liquid phases [25]. Some results on HAT4 and its composite are reported in our earlier publication [26].

2. Experimental section

The Cu–NPs (~50 nm) have been procured from Sigma Aldrich with purity greater than 99.5%. It has been used for DLC nano-composite without any further treatment. HAT4 + 0.6 wt.% Cu–NP composite has been prepared by adopting the dispersion method using an ultrasonicator coupled with heater. Shimadzu Analytical Balance has been used for weighing precise amount of all the materials. HAT4 dissolved completely while Cu–NPs are imposed to dissolve in chloroform. Both the solutions have been mixed together and ultrasonicated for 1 h. The room temperature evaporation of solution removes chloroform and finally yields dry mixture for further characterizations. The thermodynamic parameters such as phase transition temperatures, associated enthalpies and entropies have been determined in heating and cooling process by Differential Scanning Calorimeter (DSC) of NETZCSH'S (model DSC-200F3-Maia). Thermograms have been recorded in temperature range of 30–160 °C at various scan rates from 2.5 to 15.0 °C/min with the interval of 2.5 °C/min.

For dielectric study, the test cell was prepared by two Indium tin oxide (ITO) coated glass plates of sheet resistance ~25 Ω/□. Gap of 10 μm has been fixed by using mylar spacers between two ITO plates. The dielectric data have been acquired by Alpha-A High Performance Frequency Analyser from Novo Control technologies coupled with two-wire Impedance Interface ZG2 in the frequency range of 10 Hz to 40 MHz. The temperature of the sample has been controlled with the help of a hot stage (Instec's USA model HS1). Temperature near the sample has been determined by measuring thermo-emf of a copper-constantan thermocouple with the help of a six and half digit multimeter from Agilent (model-34410A) with the accuracy of ± 0.1 °C. The active capacitance of test cell (C_A) has been determined by the standard method described earlier [27]. The HAT4 and its nanocomposite were filled in its isotropic liquid phase at 10 °C above of their clearing point. Samples were cooled slowly (@0.1 °C/min) from the isotropic phase to get homeotropic alignment. The relative permittivity and conductivity of the samples have been determined by the standard relationships [27,28].

UV–vis absorption spectra of pure HAT4 and mixture have been recorded by UV-1800 Shimadzu recording spectrophotometer within the wavelength range of 190–900 nm with the accuracy of ± 0.3 nm. Standard rectangular quartz cells of 10 mm path length have been used for the measurement and chloroform is taken as reference solution. The sample solution has been taken as dilute as possible to reduce the flattening effect of absorption spectra. The maximum uncertainty in the measurements of transition temperatures by DSC is ±0.1 °C and in transition enthalpy is ±1%. The uncertainty in the measurements of dielectric permittivity and conductivity is less than ± 3%.

3. Results and discussion

3.1. Thermodynamic studies

The DSC thermograms of pure HAT4 and its copper nanocomposite (HAT4 + CuNPs) at the scan rate of 2.5 °C/min are shown in Fig. (2). The transition temperatures (see Fig. 2) for crystal (Cr) to columnar hexagonal (Col_{hp}) and Col_{hp} to isotropic (Iso) phase of pure HAT4 are in good agreement with the literature [29]. It is expected that at the melting point (i.e. transition temperature from crystal to mesophase), the alkyl chains of molecular crystals melt and provide fluidity to the mesophase while at the clearing point (i.e. transition temperature from mesophase to the isotropic liquid) the unstacking of the central cores convert it into an isotropic liquid state [13]. From Fig. 2, it is clearly seen that the dispersed Cu–NPs demonstrate negligible effect on transition temperatures of the pure material. However, due to the inclusion of Cu–NPs, temperature range of Col_{hp} phase in the cooling cycle has marginally enhanced by ~0.9 °C (see value of transition temperatures given in the following lines). It has been observed that the peak transition temperatures vary linearly with the scanning rate in heating and cooling cycles as usual, which happens because of the finite thermal resistance between sample and an oven under nonequilibrium condition when system is dynamic. The transition temperatures (i.e. peak points) and transition enthalpies (both in parenthesis) along with phase sequence of HAT4 and its CuNP composite at 2.5 °C/min scan rate in heating and cooling cycle are as follows:

Pure HAT4

Heating cycle: Cr → (87.4 °C, ΔH = 32.5 J/g) → Col_{hp} → (145.5 °C, ΔH = 28.5 J/g) → Iso

Cooling cycle: Iso → (143.7 °C, ΔH = 28.1 J/g) → Col_{hp} → (79.3 °C, ΔH = 19.2 J/g) → Cr.

HAT4 + 0.6 wt.% CuNPs

Heating cycle: Cr → (87.2 °C, ΔH = 30.9 J/g) → Col_{hp} → (145.4 °C, ΔH = 25.5 J/g) → Iso

Cooling cycle: Iso → (143.9 °C, ΔH = 25.8 J/g) → Col_{hp} → (78.6 °C, ΔH = 13.5 J/g) → Cr.

The values of transition enthalpy and entropy for Cr (perfectly ordered phase)-Col_{hp} (partially ordered phase) and Col_{hp}-Iso (completely disordered phase) transitions decreases in heating and cooling cycles both for HAT4-NP composite as compared to pure HAT4. These data support that the CuNPs enhance the stability of partially ordered Col_{hp} phase of HAT4.

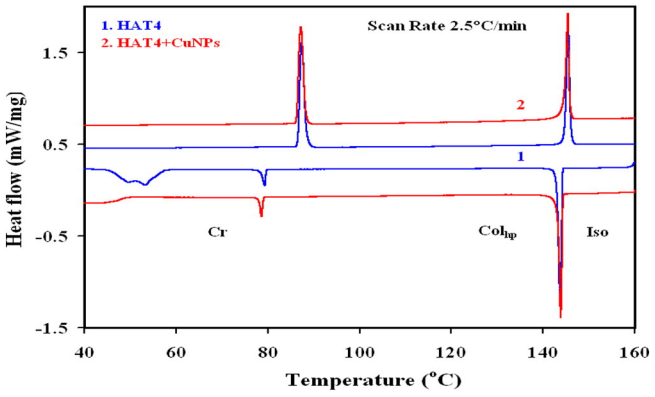

Fig. 2. DSC thermograms of pure HAT4 and its 0.6 wt.% CuNP composite in the heating and cooling cycles. Curve 1 represents pure HAT4 and curve 2 represents HAT4 + CuNPs at the scan rate of 2.5 °C/min.