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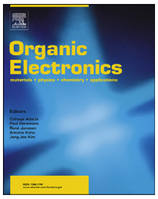

Homologous binary mixtures and improved hole conduction of self-assembled discotic liquid crystals

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Discotic liquid crystals (DLCs) are considered promising materials for organo-electronic applications. Columnar alignment of DLCs leads to anisotropic charge transport with high charge carrier mobility. However, pure DLCs exhibit low intrinsic charge carrier density which limits bulk conductivity. This research studies the alignment and conductivity properties of small molecule triphenylene-based DLCs to develop hole transport layers for potential applications in organic semiconductor devices. Binary mixtures of homologous DLCs of the hexakis(n-alkyloxy)triphenylene series (HAT6 and HAT10) are formulated. Mesophase characteristics and columnar alignment of these mixtures are characterized using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Alignment, orientation and order of columnar packing in the mixtures is studied using X-ray diffraction (XRD) and grazing incidence wide angle X-ray scattering (GIWAXS) measurements. It is identified that binary mixture formation strongly effects the columnar alignment in solution processed films. Furthermore, to increase charge carrier density in the DLC films a strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) is added as a p-type dopant, followed by an extensive characterization of its doping effect. POM, DSC thermal scans, UV–visible spectroscopy, photo-luminescence spectroscopy (PL) and I-V measurements are utilized to characterize and establish the improvement of hole conduction in the doped films. It is observed that F4TCNQ-doped triphenylene DLC films exhibit two-fold increase in hole conductivity, making the materials highly relevant for charge transport applications.

1. Introduction

Discotic liquid crystals (DLCs) typically exhibit columnar mesophase characteristics, where the mesophase exists in a given temperature range [1]. DLCs were first discovered in 1977 by Chandrasekhar [2,3] while he was working with hexaesters of benzene. Since then, DLCs have been studied extensively from both fundamental and application perspectives [4–7]. The mesophases are typically comprised of disc-shaped molecules that form molecular columns due to phase segregation of the aromatic and aliphatic segments, in addition to π-π interactions between the poly-aromatic molecular condensed cores. Individual poly-aromatic molecules exhibit significant pi-conjugation, and overlap within well-aligned molecular columns have motivated significant efforts to realize their potential as self-assembled organic semiconductors [2,4,8–11].

Organic semiconductors have been an area of keen interest for several decades now, with some of the earliest successful investigations dating back to 1956 [12]. The possibility of having semi-conducting solution processed materials that can be easily and cheaply deposited at low temperatures to fabricate optoelectronic devices such as organic light emitting diodes (OLEDs) [13], organic solar cells [14–16] and field-effect transistors [17] is very appealing for industrial applications. The underlying physical

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principles that makes almost all types of organic semiconductors (polymeric and small molecule) possible is bond conjugation (alternating π-σ bonds), that leads to the splitting of molecular energy levels, to induce band-like energy levels: conduction (lowest unoccupied molecular orbital (LUMO)) and valence (highest occupied molecular orbital (HOMO)) [18].

DLC molecules typically have conjugated aromatic cores, with substituted alkyl-chains that induce liquid crystalline (LC) behaviour. Numerous different families exist based on varying polyaromatic cores, such as triphenylene [19], pyrene, porphyrin [20], phthalocyanine, and hexabenzocoronene [21]. The inter-molecular packing of DLC materials is important in determining the charge transport mechanism of the materials in optoelectronic applications. As an example, the distance between adjacent aromatic cores in the LC state of hexahexyloxytriphenylene (HAT6) is estimated to be about 3.5 A°, which is short enough to enable charge carrier hopping between molecules along the columnar axis. However, the intermolecular gap is too wide to favour band-like conduction [4,22]. Charge hopping (transport) is only favourable along the columnar axis and the alkyl chains then act as insulating spacers, leading to orientational anisotropy in the effective charge carrier mobility and conduction. This anisotropy has been measured previously [23] and can be imagined of as the self-assembly of molecular wires along the columnar direction, where the individual columns are insulated from each other through the alkyl side-chains. This intrinsic electrical conductivity anisotropy of columnar DLCs is potentially useful for device applications, but the key to proper utilization lies in the ability to control the orientation of the molecular columns in both the LC (liquid crystalline phase) and Cr (crystalline phase). Two of the most common orientations are described with respect to the columnar axis (director), either parallel (planar) (Fig. 1f), or perpendicular (homeotropic) (Fig. 1e) to the plane of the substrate.

It has been demonstrated that DLCs typically exhibit high charge carrier (typically hole) mobility [21,24], and an increase in the aromatic core size of the constituent molecules increases the charge carrier mobility. However, LC molecules with larger aromatic cores have higher LC to isotropic (I) transition temperatures, poor solubility, are less desirable for capillary filling through melt processing. In this study, we use triphenylene-based DLCs, that have a relatively small core size ($\Sigma\mu \approx 0.002$ cm^2 V^{-1} s^{-1} in the LC phase [21], with four fused benzene rings in the aromatic core). However, they demonstrate a low melting and clearing point, allowing low temperature melt processing.

One of the commonly utilized and highest performing small molecule for hole transport layer applications is 2,2′,7,7′-tetrakis-(*N*,*N*-di-4-methoxyphenylamino)-9,9’-spirobifluorene (Spiro-OMeTAD). It has recently been shown that Spiro-OMeTAD can be doped with dicationic Spiro salts to increase the material conductivity to ~1×10^{-1} S/m [25], up from conventional Lithium salt doped Spiro-OMeTAD that typically yielded conductivity of the order of ~1×10^{-3} S/m [26]. The highest value of hole mobility in doped Spiro film ever reported is of the order of 10^{-4} cm^2/Vs [27], this is in fact lower than the hole mobility in triphenylene HAT6 (10^{-3} cm^2/V) [21]. So, combined with the higher mobility, smaller molecular size, lower melting temperatures and higher control of alignment properties, there is significant motivation to improve the conductivity of triphenylene DLCs to yield competitive, and possibly better hole transport layers.

In this study we focus on both the alignment and conductivity of hexakis (n-alkyloxy)triphenylene DLC derivatives HAT6 and HAT10 in the plastic crystalline (Cr) phase [28]. As these materials crystallize at room temperature, understanding and controlling the alignment in the LC-Cr transition upon cooling is critical. Local defects at domain boundaries can trap charge carriers, leading to lower charge carrier mobilities [29]. Significant work has been

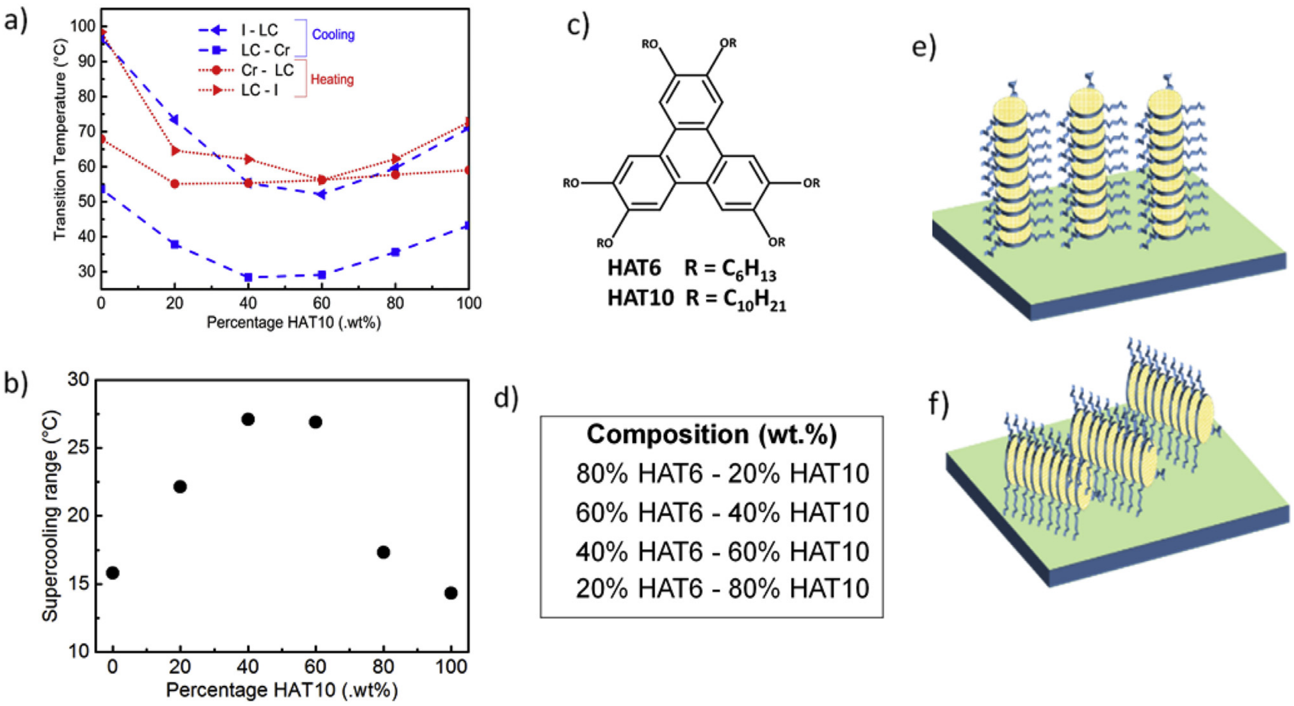

Fig. 1. Plots of phase transition temperatures of HAT6 - HAT10 binary mixtures on heating (red lines) and (b) cooling (blue lines), extrapolated from DSC thermal scans (5 °C/min). (b) Illustrates the super-cooling effect in binary mixtures of HAT6-HAT10. Data points have been quantified by the difference between the crystallization (LC-Cr) and melting (K-LC) transitions. (c) illustration of the chemical structure of HAT6 and HAT10. (d) Summary of the binary mixture compositions prepared using HAT6 and HAT10. (e), (f) Schematics of the two most common alignment directions of columnar DLC phases, with (e) homeotropic alignment, director normal to substrate, and (f) planar alignment, with columnar director parallel to substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)