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The influence of the nematic phase on the phase separation of blended organic semiconductors for photovoltaics



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ABSTRACT

Differential scanning calorimetry in combination with atomic force microscopy is used to examine the phase separation of a blended nematic liquid crystalline electron-donor and crystalline perylene electron-acceptor mixture. Separate domains of donor and acceptor material are mostly retained in the blend, although a small proportion of the acceptor, increasing with increasing donor concentration, is mixed in with the donor domains. Annealing in the nematic phase allows the donor and acceptor molecules to move and generate phase-separated domains of the required size, thus enhancing the performance of bulk heterojunction photovoltaic devices based on these blends. We show that the optimum annealing temperature can be controlled by manipulation of the temperature range of the nematic phase of the donor.

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1. Introduction

Columnar, smectic and, more recently, nematic liquid crystals have been shown to be very promising charge-transporting organic semiconductors due to their ability to spontaneously self-assemble into highly ordered domains in uniform, thin films over large areas [1–3]. This combination of properties allied with broad absorption spectra render them particularly suitable as active materials for organic photovoltaics, such as bulk heterojunction devices based on blends of liquid crystalline electron donors and crystalline electron acceptors. Photogenerated excitons are dissociated at the interface between the phase-separated domains of the donor and acceptor components. The separated electrons and holes then travel along different and distinct continuous pathways in opposite directions to the electrodes. Photovoltaic cells comprising a coronene compound as a donor with columnar liquid crystalline phases blended with an electron acceptor showed power conversion efficiencies up to 1.5% under standard measurement conditions [4–6]. The performance of these organic photovoltaic (OPV) cells was optimized by effective use of thermal annealing to control the degree of molecular ordering

within the individual domains of electron donors and electron acceptors. Thienothiophene polymers, which have high-temperature liquid crystalline phases, were blended with soluble fullerene derivatives [7,8], with optimized devices having a power conversion efficiency of 2.5%. It is noted that annealing in the liquid crystal phase improved the performance of photovoltaic devices incorporating donors with either columnar or lamellar polymeric phases [6,9,10]. A nematic liquid crystal composite with a porous surface and sub-micron scaled grooves has also been used to provide a distributed interface to vertically separate electron-donating and electron-accepting films in a bilayer PV device [11,12]. However, quite surprisingly, the use in OPVs of low-molar-mass nematic liquid crystals (small molecules) has not been studied to any significant degree [13]. The nematic phase of such compounds possesses a much lower viscosity than that of either highly ordered columnar liquid crystals or high molecular weight liquid crystalline polymers, which are exceptionally viscous materials. Therefore, nematic liquid crystals should offer significant advantages in controlling the morphology of the donor–acceptor composites for organic photovoltaics, especially when using thermal annealing to control domain size and morphology.

This work addresses the important question of how the self-assembly properties of liquid crystals can be exploited to control the morphology of the donor–acceptor composites for organic photovoltaics. Our model system consists of a nematic donor blended with a crystalline perylene based acceptor. We propose

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a combination of macroscopic and nanoscale techniques, differential scanning calorimetry and atomic force microscopy, as an effective method to investigate how the liquid crystalline phase is modified by blending and whether the donors and acceptors are intimately mixed or occupy distinct domains. We examine why annealing in the nematic phase improves morphology and optimises PV performance. We choose two distinct donor–acceptor blends, where both LC donors are electrically and optically very similar but have significant different LC temperature ranges, to confirm the relevance of the LC phase.

2. Experimental

Table 1 shows the chemical structure of the materials used in this investigation. The synthesis of the electron-donor materials 1 and 2 is described in the Supplementary information. The synthesis of perylene acceptor 3 has been reported previously [12]. Cyclic voltammetry and absorption spectroscopy are used to obtain the ionization potential and electron affinity of the materials, as discussed in the supplementary information.

A Perkin-Elmer differential scanning calorimeter (DSC 7) was used to measure the phase transition temperatures of the pure materials and blends, which are summarized in Table 2. Blends were prepared by dissolving either donor 1 or donor 2 along with the appropriate amount of acceptor 3 in dichloromethane as a solvent and then drop-casting the resultant solution into a standard aluminium differential scanning calorimetry (DSC) pan (Perkin-Elmer) using a pipette. Around 4–5 mg of material was used for each DSC sample. The pan was prepared in this way in order to simulate the blend mixture produced during thin film processing. Donor 1 and acceptor 3 were mixed in a 1:3 mol ratio, whilst donor 2 and acceptor 3 were mixed in mole ratios of 4:3, 1:1, 1:2 and 1:3. A standard indium sample was used to calibrate the DSC prior to all measurements. The scan rate was $10\text{ }^{\circ}\text{C min}^{-1}$ and two heating–cooling cycles were performed for each blend. The morphology of the blended thin films was investigated with an Atomic Force Microscope (AFM) developed by Molecular Imaging (Agilent) in the tapping mode. MAC Levers Type II cantilevers (Agilent) were used for all measurements. Picoscan V.5.2 was used to produce the images, RMS roughness and height distribution data. Fast Fourier Transforms (FFT) and the power spectral density data (PSD) were obtained using Gwyddion free-ware software. We investigated areas of $5 \times 5\ \mu\text{m}^2$ and $1 \times 1\ \mu\text{m}^2$, each area being composed of 1024×1024 data points.

Soda lime glass substrates were provided by UQG optics with a 100 nm thick indium tin oxide (ITO) layer, giving a sheet resistance of $\leq 20\ \Omega/\text{sq}$. Acid etching was used to remove strips of ITO from the edges to allow contact to the cathode. The substrates were cleaned by sonification and treated with oxygen plasma.

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) supplied by Baytron (P AI4083) was sonicated for 5 min, spin cast onto the ITO substrate at 4000 rpm for 30 s and then annealed at $120\text{ }^{\circ}\text{C}$ for 30 min followed by 5 min at $220\text{ }^{\circ}\text{C}$. The active layer was spincoated from 1.5% by weight solution of the donor and acceptor compounds mixed in various mole ratios in chlorobenzene at 2000 rpm for 30 s. This was followed by annealing on a hot-plate under various conditions as described later. The cathode consisted of a thin layer ($\sim 0.6\text{ nm}$) of lithium fluoride (LiF) and a layer (100 nm) of aluminium deposited by thermal evaporation under vacuum. The completed PV device was mounted in a vacuum sealed test chamber for characterisation outside a glove box. The devices were illuminated with a Xenon lamp (Bausch & Lomb), dispersed through a monochromator and attenuated with neutral light filters over an area of 0.25 cm^2 . The current–voltage characteristics of the photovoltaic devices were measured in an inert atmosphere using a Visual-Basic controlled picoammeter.

3. Results and discussion

3.1. Phases of binary donor–acceptor mixtures

The ionization potential and electron affinity of liquid crystalline compounds 1 and 2 are the same (5.52 eV and 3.15 eV, respectively) within experimental error. Both of them act as electron donors, when blended with the crystalline electron acceptor 3, see Table 1, which has an electron affinity of 4.19 eV. Fig. 1 shows the DSC traces for the donors 1 and 2 and the acceptor 3, the blend comprising 2 and 3 as well as the blend 1 and 3 in a 1:3 mol ratio. The transition temperatures of these compounds and their blends, as well as those of other blends of 2 and 3 with different mole ratios, are summarised in Table 2.

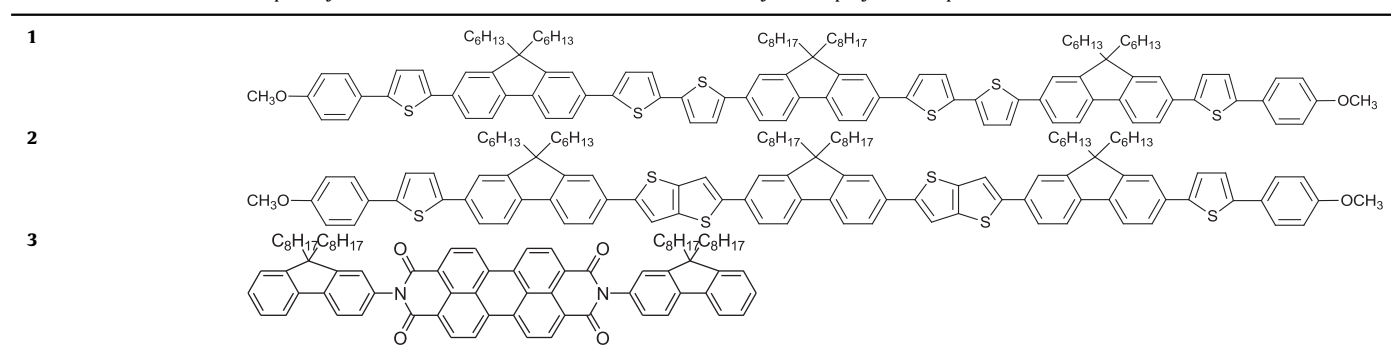
Table 2

The glass transition temperature (t_g), melting point (Cr–N and Cr–I), clearing point (N–I) and recrystallisation temperature (I–Cr) for each of the four blends studied. The fifth column records the enthalpy of melting (ΔE , per gram) of the acceptor molecule 3.

| Material | Blend molar ratio (D:A) | t_g ($^{\circ}\text{C}$) | Cr–N ($^{\circ}\text{C}$) | Cr–I ($^{\circ}\text{C}$) | ΔE (J/g of 3) | N–I ($^{\circ}\text{C}$) | I–Cr ($^{\circ}\text{C}$) |
|----------------|-------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------|----------------------------|-----------------------------|
| 1 | | 80 | | | | 218 | |
| 2 | | 94 | 180 | | | 303 | |
| 3 | | – | – | 274 | 19.1 | – | 256 |
| 2 and 3 | 1:3 | 93 | 180 | 256 | 16.4 | – | 209 |
| | 1:2 | 93 | 180 | 257 | 11.5 | – | 206 |
| | 1:1 | 94 | 181 | 250 | 10.4 | – | 181 |
| | 4:3 | 94 | 180 | 250 | 8.7 | – | 180 |
| 1 and 3 | 1:3 | 80 | – | 265 | 10.1 | 206 | 225 |

Table 1

The chemical structure of the liquid crystalline electron-donor materials 1 and 2 and the crystalline perylene acceptor 3.



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