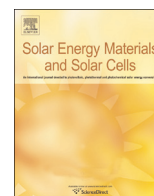




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# The effect of mesomorphology upon the performance of nanoparticulate organic photovoltaic devices



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## ABSTRACT

Scanning transmission X-ray microscopy (STXM) compositional mapping has been used to probe the mesomorphology of nanoparticles (NPs) synthesized from two very different polymer:fullerene blends: poly(3-hexylthiophene) (P3HT); phenyl-C61-butyric acid methyl ester (PCBM) and poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl] (PSBTBT); PCBM. The STXM data shows that both blends form core-shell NP structures with similar shell compositions, but with different polymer:fullerene ratios in the core regions. P3HT:PCBM and PSBTBT:PCBM NP organic photovoltaic (OPV) devices have been fabricated and exhibit similar device efficiencies, despite the PSBTBT being a much higher performing low band gap material. By comparing the measured NP shell and core compositions with the optimized bulk heterojunction (BHJ) compositions, we show that the relatively higher performance of the P3HT:PCBM NP device arises from the fact that its shell composition is much closer to the optimal BHJ value than that of the PSBTBT:PCBM NP device.

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## 1. Introduction

The incorporation of nanoparticle (NP) organic thin films into organoelectronic devices is a rapidly developing area of research as they offer significant potential advantages over conventionally processed organic thin films. The materials may be processed from aqueous dispersions eliminating the safety and cost issues associated with large scale processing from organic solvents [1,2]. More importantly, the nanoparticulate structure offers the opportunity to control the semi-conducting polymer and blend morphology on the nanoscale [3,4]. Consequently, NP organic thin films are increasingly finding application in areas such as thin film transistors [5], light-emitting diodes [6], and in particular

*Abbreviations:* OPV, organic photovoltaic; PCE, power conversion efficiency; NP, nanoparticle; P3HT, poly(3-hexylthiophene); PSBTBT, poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl]; PCBM, phenyl C61 butyric acid methyl ester; SDS, sodium dodecyl sulfate; ITO, indium tin oxide; STXM, scanning transmission X-ray microscopy; TEM, transmission electron microscopy; SEM, scanning electron microscopy; DLS, dynamic light scattering; BHJ, bulk heterojunction

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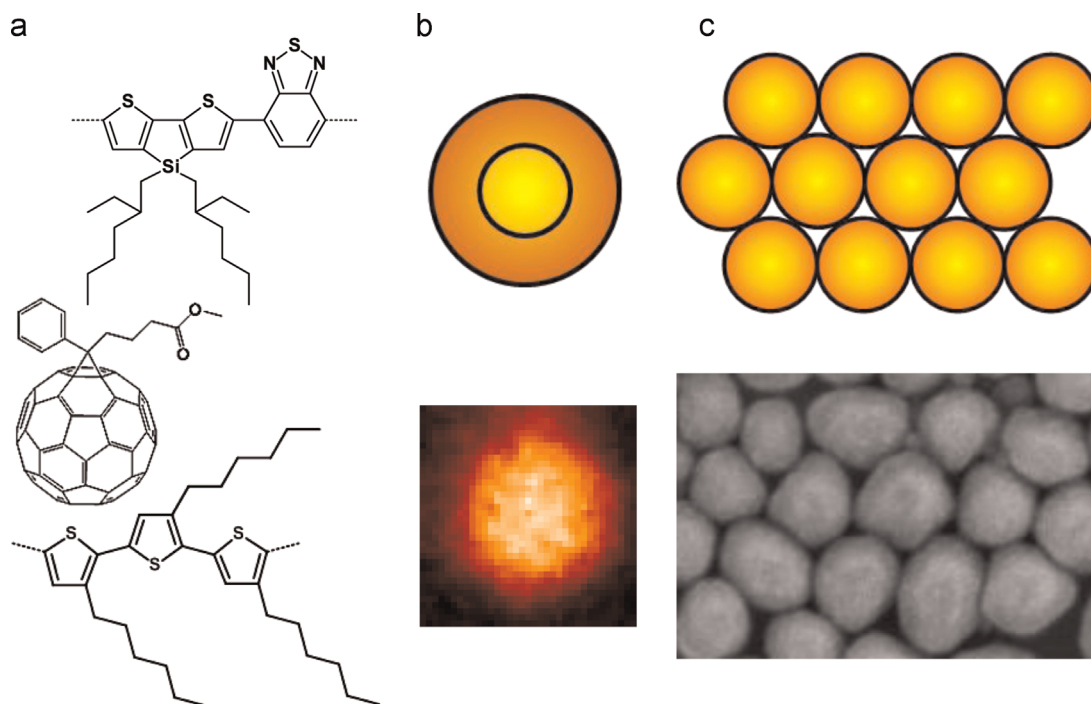
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photovoltaics [7,8] where roll to roll printing of NP OPV devices has been demonstrated [9,10] and power conversion efficiencies (PCEs) of up to 2.5% have already been achieved for small area devices [11].

Over the past few years, advanced microscopic techniques have revealed that conventional bulk-heterojunction (BHJ) active layers are structured on a hierarchy of length scales; ranging from atomic level interactions between component molecules/polymers (sub-nm) to the formation of ordered domains (a few tens of nm) to surface energy driven large scale phase segregation (up to microns) [12]. The precise nature of the material interactions on all of these length scales is critical to device function; if any of them are detrimental device performance suffers. In BHJ devices, the ordering on all of these length scales is driven by the material thermodynamic properties and can only be indirectly influenced by experimental levers [13]. Consequently, optimization of the device structure occurs primarily via trial and error and is empirically determined for each material system.

Uniquely, the NP approach confines device structure on three length scales: (a) molecular/polymer interactions on the nanometer scale (the nanoscale), (b) internal structure of the NP on the scale of a few tens of nanometers (the mesoscale) and (c) the



**Fig. 1.** A schematic showing the three length scales on which material interactions occur within the NP approach: (a) the nanoscale (1–10 nm, demonstrated by skeletal formulae of PSBTBT, PCBM and P3HT from top to bottom), (b) the mesoscale (10–100 nm demonstrated by the core-shell nanoparticle structure of a 1:1 P3HT:PCBM nanoparticle observed via scanning transmission X-ray microscopy (STXM)) and (c) the macroscale (> 100 nm demonstrated by the hexagonal close-packing in 1:1 P3HT:PCBM nanoparticles observed via transmission electron microscopy (TEM)).

arrangement of NPs in the active layer film (the macroscale) (Fig. 1).

Researchers have begun to understand the structural motif of the nanoparticles themselves [3,4]; revealing that the NPs typically have core-shell structures where the core and shell differ in blend composition [3]. However, little work has been undertaken to determine how the nature of the semiconducting materials determines this mesomorphology and how it then influences the performance of the NP OPV devices.

In this paper, we investigate the mesomorphology and device performance of NP OPV devices for two very different polymer:fullerene blends: poly(3-hexylthiophene) (P3HT): phenyl-C61-butyric acid methyl ester (PCBM) and poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl] (PSBTBT): PCBM. These polymer:fullerene blends have been shown to produce BHJ OPV devices with PCEs in the 3–5% and 4–6% ranges, respectively, and with an active layer phase segregation which is near optimal for charge generation. Here we show that the materials dictate the mesomorphology of the NPs. Using scanning transmission X-ray microscopy (STXM), we show how the composition of the core and shell regions dictates the performance of the NP devices, even though the structures are very similar for the two blend systems. In particular, we demonstrate that controlling the composition of the shell is critical in realising the full potential of a given material system.

## 2. Results and discussion

In order to investigate and understand the effects that the active layer components have upon NP mesomorphology, NPs were fabricated from two different polymer:fullerene blends. A 1:1 P3HT:PCBM blend was chosen as the first material system since it is the most studied system in the literature [14], with the material properties of the components and blend, and the physical

properties and performance of the resulting OPV devices well established [14].

A 1:1 PSBTBT:PCBM blend was chosen as the second material system since it is representative of the recently developed low band gap polymers for OPV devices [15,16], and has shown promise in tandem OPV devices [17,18]. Whereas P3HT is a largely amorphous polymer in the as-spun state and must be thermally treated to produce a more crystalline material [19,20], in contrast PSBTBT is a highly crystalline polymer [15,21–23]. Upon blending with a fullerene, PSBTBT:fullerene blends display excellent charge transport properties, with little recombination occurring [23].

Static water contact angles for P3HT ( $106 \pm 0.3^\circ$ ) [24], PSBTBT ( $104.3^\circ$ ) [23] and PCBM ( $50.6^\circ$ ) [23] have been reported. While contact angles for conducting polymers are highly dependent upon the level of doping of the polymer sample, these values indicate that the surface energy of PSBTBT is similar to that of P3HT. Consequently, PSBTBT would be expected to form core-shell NPs in a PCBM blend in the same way that P3HT does, with a polymer-rich shell and a fullerene-rich core.

Nanoparticles of 1:1 blends of both P3HT:PCBM and PSBTBT:PCBM were prepared using the standard miniemulsion method reported in the literature [7]. As discussed elsewhere [25], particles of two size ranges were prepared for device characterization and scanning transmission X-ray microscopy (STXM) measurements by varying the amount of surfactant added to the emulsion. Fig. 2 shows plots of the size of these particles as extracted from TEM images by a circular Hough particle screening algorithm. For P3HT:PCBM mean particle diameters of  $23.8 \pm 7$  nm and  $127 \pm 29$  nm are observed for the small and large particles, respectively, and for PSBTBT:PCBM particles, mean particle diameters of  $23.5 \pm 7$  nm and  $104 \pm 34$  nm, are observed for small and large particles. The error refers to the standard deviation of the particle distribution.

Figs. 3 and 4 show transmission electron microscopy (TEM) and STXM images for both the large PSBTBT:PCBM and P3HT:PCBM particles, respectively. The TEM images confirm that both sets of

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