

# Effect of a high boiling point additive on the morphology of solution-processed P3HT-fullerene blends



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## ABSTRACT

The use of high boiling point additives in solution processing has been widely employed to control the active layer morphology in bulk heterojunction organic solar cells. The morphology of the heterojunction is crucial in controlling charge separation and extraction by the electrodes, and therefore the power conversion efficiency (PCE) of the device. This paper presents a study of time-resolved fluorescence quenching in blends of P3HT containing varying concentrations of the fullerenes PC<sub>61</sub>BM or PC<sub>71</sub>BM. The relationship between the fluorescence quenching rate and fullerene concentration indicates that the fullerene molecules are dispersed within the P3HT film for up to 5% by mass of fullerene. For higher fullerene concentrations, the additional fullerene molecules aggregate and form fullerene domains. The high degree of phase segregation observed in these blends is beneficial for solar cell performance because the segregated fullerene phase provides electron percolation pathways through the blend. The addition of 1,8-diiodooctane (DIO) to the solutions for spin coating into films changes the scale of fullerene segregation when the ratio by mass of fullerene exceeds 20%. At high fullerene concentrations the rate of fluorescence quenching decreases in P3HT:PC<sub>61</sub>BM blends when prepared with DIO indicating a larger scale phase separation. The effect of DIO on the morphology of P3HT:PC<sub>71</sub>BM blends is the opposite in that it causes faster quenching in the blends. Overall the results show that DIO can be used to control the morphology of photovoltaic blends of P3HT with fullerenes.

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## 1. Introduction

Conjugated polymers are promising materials for solar cells. When incorporated in bulk heterojunction organic photovoltaic devices, they are capable of producing power conversion efficiencies (PCEs) of over 10% [1,2]. Nanocomposite blends consisting of a conjugated polymer and fullerene derivative are often used as active layers which are of great potential for solar cells due to being easily processable from solution. This also allows them to be inexpensively deposited on flexible substrates at low cost. In addition, they are lightweight, have a high absorption coefficient ( $\sim 10^5 \text{ cm}^{-1}$ ) and flexible [3–5]. Absorption of light by a conjugated polymer leads to the generation of a bound electron–hole pair known as an exciton, which must be separated into its constituent charges in order to produce an electric current. This is achieved by blending the conjugated polymer – which acts as the donor – with an acceptor of higher electron affinity, such that the electron is then transferred to the acceptor. The dissociation of the exciton occurs at the donor–acceptor heterojunction, so it is important to

ensure all light-absorbing sites in the polymer are within reach of the heterojunction. Therefore the morphology of the heterojunction interface coupled with knowledge of the exciton diffusion length (typically on the scale of  $\sim 10 \text{ nm}$ ) [6,7] in the polymer are important parameters in understanding and optimising the rate of charge generation in organic photovoltaic devices.

Exciton dissociation depends on the shape of the donor–acceptor heterojunction interface available to the exciton, which is influenced by the morphology of the active layer within the device structure. In many devices, a donor–acceptor bulk heterojunction is employed in order to be able to optimise the interfacial area [8–11]. To create a bulk heterojunction, the donor and acceptor are dissolved in a solvent, and then deposited onto a substrate to form an intermixed nanocomposite blend with a high surface-area per volume for the interface. The large surface area of the bulk heterojunction bears an advantage over a planar heterojunction, and results in excitons in the donor having an increased chance of encountering the interface. It is also important, however, that within a bulk heterojunction, continuous pathways are maintained such that the separated electron and hole are able to reach the interface before recombination occurs. These factors are considered when optimising the morphology of the bulk heterojunction,

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which endeavors to strike a balance between the two by achieving a phase separated interpenetrating bicontinuous network of the donor and acceptor in the blend. In this way, the morphology of the active layer is important in that it determines the rates of exciton diffusion and charge generation within the device. The molecular structure within either the donor or the acceptor phase directly affects light absorption and carrier mobility during the photovoltaic process, whilst the scale of phase separation between the donor and acceptor phases – in which domains are formed from the acceptor phase – controls the surface area of the donor–acceptor interface at which dissociation of the excitons occurs, and the distance excitons need to diffuse to encounter an acceptor [9–12]. Overall, the active layer morphology is seen to crucially impact the performance of the photovoltaic device [9,10,13–15].

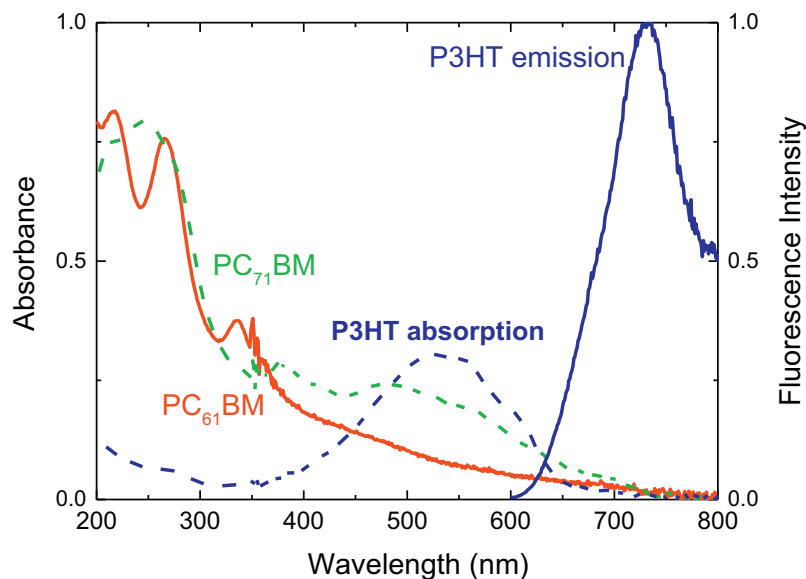
Measuring the morphology is challenging due to the small lengthscales encountered. Techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) have previously been employed to measure the nanoscale morphology of polymer thin films [15,16]. Although such methods have successfully probed the nanoscale morphology in film blends of other polymers – such as PTB7 – with fullerene, in the case of P3HT, the possibility of measuring the dimensions of domain networks formed during phase separation is obstructed by the lack of variation in the hardness of the constituent materials. This makes it difficult to distinguish between the donor and acceptor phase and therefore to make a measurement of their dimensions. Therefore attention has turned to searching instead for indirect methods for probing the morphology in a polymer fullerene blend. Research has demonstrated that the active layer morphology is heavily dependent on the processing steps and solvents used during the deposition. Various processing techniques have been developed in order to control and optimise the morphology. One processing method used is thermal annealing, which involves heating of the active layer at a defined temperature (which occurs between 100 and 130 °C for P3HT) for a finite amount of time [17]. Annealing has been observed to induce separation of the donor and acceptor phases, with the latter forming domains of approximately 10 nm [18–21]. It has been shown that thermal annealing leads to an enhancement in the PCE of devices incorporating P3HT–fullerene blends [22], due to crystallisation of the P3HT or to an enhancement in the morphological structure of the film with

larger fullerene domains being formed [8,23]. Another method which has been employed is exposure of the deposited active layer to solvent vapors [24,25]. Recent research has focused on additive processing, due to the improvement in power conversion efficiency observed with the inclusion of solvent additives within the film blends [12,26–28]. Processing of films with the addition of 1,8-diiodooctane (DIO) has been noted as a successful method for improving conversion efficiency in a bulk heterojunction solar cell, with an increase in the internal quantum efficiency by a factor of 2 having been observed [15,29,30].

In this paper, time resolved photoluminescence is measured in polymer–fullerene blends of P3HT:PC<sub>61</sub>BM and P3HT:PC<sub>71</sub>BM, in order to study how the rate of exciton harvesting is affected by an increase in the acceptor concentration. Solar cells with active layers fabricated from P3HT:PC<sub>61</sub>BM have demonstrated PCEs of up to 5% [12]. This paper uses time-resolved fluorescence to understand the significance of morphology within the polymer fullerene blends on charge generation in the device. The effect of additive processing on the fluorescence is analysed in order to understand how the morphology of the donor–acceptor interface – and therefore the rate of exciton dissociation – is affected.

## 2. Experimental methods

The materials incorporated within the film blends consisted of P3HT with regio-regularity 91–94% obtained from Rieke Materials (item number 4002-EE), and PC<sub>61</sub>BM and PC<sub>71</sub>BM from Solenne. Film samples were prepared by spin-coating solutions onto fused silica substrates. The solutions for spin-coating were made from stock solutions of P3HT (with concentration 20 mg/ml) and of PC<sub>71</sub>BM and PC<sub>61</sub>BM (each with concentrations 0.2 mg/ml, 2 mg/ml and 10 mg/ml.) which were prepared in a nitrogen glovebox using anhydrous chlorobenzene. The stock solutions were stirred overnight at 40 °C. To prepare the solutions for spin-coating into films, the volume of P3HT was fixed whilst the amount of fullerene solution was varied. Firstly, films without additive were spun onto clean fused silica substrates. Then 3% by volume of 1-8-diiodooctane (from Sigma–Aldrich) was added to each of the solutions and stirred for 30 min before spin-coating onto a new set of cleaned silica substrates. The deposited films were then dried for 2 h in an evaporator under high vacuum.



**Fig. 1.** The absorption spectra for PC<sub>71</sub>BM (green) and PC<sub>61</sub>BM (red) and P3HT (dark blue), alongside the fluorescence spectrum for P3HT (in blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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