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Morphological study of F8BT:PFB thin film blends

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ABSTRACT

We have studied the thin film morphology of a semiconducting polymer photovoltaic blend comprising an electron acceptor poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and the donor poly(9,9′-dioctylfluorene-*co*-bis-N,N′-(4-butylphenyl)-bis-N,N′-phenyl-1,4 phenylenediamine) (PFB). The molecular weight and blend weight ratio of the constituent polymers were used to modify the morphology. The average chemical composition of the bulk of F8BT:PFB blend in thin films was mapped using Raman microscopy at different depths from the air-film interface through controlled successive etching from the upper surface layer using an oxygen plasma. Correlating the lateral to the vertical Raman analysis of the phase separation of the film (blend weight ratio of 50:50) reveals that the μm scale de-mixed lateral phase structure seen on the free surface is present throughout most of the film thickness, though there is also some F8BT content within the PFB-rich wetting layer on the glass substrate, which we consider is due to the F8BT-rich interface at the surface to the substrate. The dependence of photovoltaic performance on morphology is discussed.

1. Introduction

Organic semiconductor photovoltaics (OPV) are actively researched because they have the prospect for low-cost manufacturing. Their operation depends on the presence of a bulk distributed heterojunction between an electron acceptor and an electron donor; this is required to separate electron hole pairs from excitons photogenerated within their diffusion range of the heterojunction [1,2]. Considerable success has been achieved using de-mixed blends of donor and acceptor, particularly when soluble derivatives of fullerene (C_{60} and C_{70}) are used as the electron acceptor. Power conversion efficiencies (PCEs) have risen rapidly [3–7] and recently PCEs of over 15% was demonstrated utilizing organic lead halide perovskites material as an active layer [8–10].

Systems made using de-mixed blends of polymers however have generally shown lower efficiencies, currently no higher than few percent [11–13]. There are two factors that may be responsible for this. Firstly, charge separation across the heterojunction seems to be relatively difficult in polymer–polymer systems; for the F8BT–PFB system studied here there is clear evidence for formation of charge-transfer excitons bound at the heterojunction that give a relatively low contribution to the photocurrent [14,15], with quantum efficiencies for charge generation of no more than a few percent. Secondly, the morphology of the de-mixed polymer–polymer materials may be less desirable than that found for polymer-fullerene systems. A good OPV device requires that the thin film morphology is of a phase separation with length scale that matches the short exciton diffusion length which is usually between 5 nm and 10 nm [16–18] and it should also contains percolation paths to transport the dissociated charge to the respective electrode. Many approaches have been used to control the morphology, such as controlling substrate temperature, different solvent, mixture of solvents, etc. [19–27]. It is important to gain a quantitative analysis of the morphology on a scale of less than 100 nm. Hence, an array of techniques has been utilized to probe the morphology of the phase separated blends in order to attain better understating of the morphology influence on the performance of photovoltaic devices [15,28–35]. Among these, Raman spectroscopy allows compositional analysis of the constituent polymers due to large Raman cross section for the modes that are coupled to π–π^* electronic excitation [29,36–39]. Most morphological studies are of the top surface of the thin film and there are few studies of the phase separation and the distribution of the material inside the bulk of the film where most of the photogeneration of excitons and charge carrier transport occurs. This study presents the tuning of the morphology and consequently the electronic properties of F8BT:PFB thin film. Firstly, the morphology is altered through a systematic variation of the

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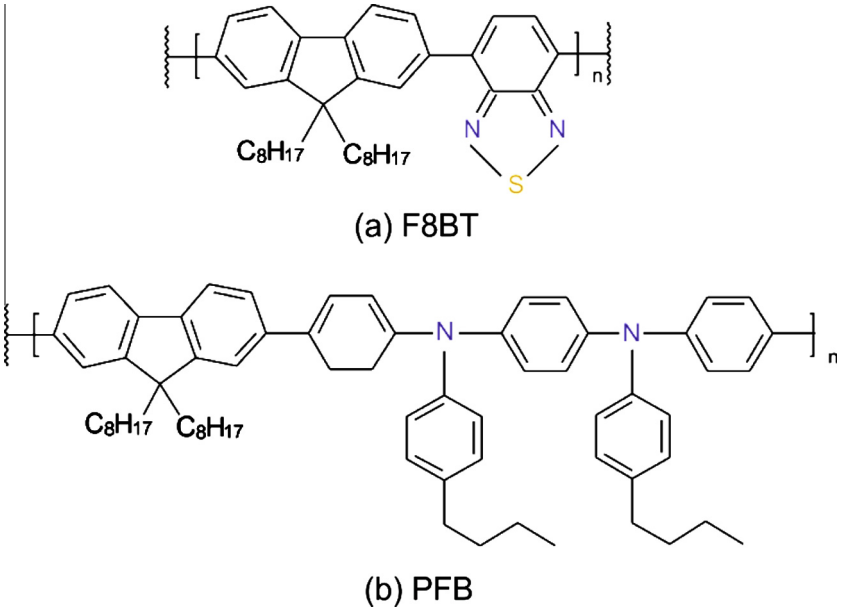

Fig. 1. The chemical structure of (a) F8BT and (b) PFB.

Table 1
The molecular weight of the investigated series of F8BT with their properties.

F8BT M_n/(kg/mol)	Degree of polymerization	Polydispersity
F8BT/9	5.7	3.45
F8BT/21	13.4	3.35
F8BT/49	31.5	1.82
F8BT/62	39.6	2.73
F8BT/90	57.5	1.99
F8BT/97	–	1.94
F8BT/129	82.4	1.77
F8BT/160	102.2	1.75
F8BT/255	162.8	1.55

F8BT molecular over an extended range (9–255 kg/mol) whilst that of PFB is kept constant. Secondly, the morphology is varied through the blend weight ratio proceeded by compositional analysis for the lateral and vertical phase separation averaged over the film thickness using Raman spectra and imaging. The results are applied to plot an image of the inner structure of the film and to interpret the performance of OPV.

2. Experimental

All materials were supplied by Cambridge Display Technology (CDT) Ltd and used without further purification. The molecular weight of PFB is 60 kg/mol while that of the studied F8BT set is shown in Table 1. The F8BT and PFB homopolymers solutions were prepared by dissolving each of homopolymers into *o*-xylene separately. Blends were then prepared with in a ratio by weight as indicated in the text. Thin films for spectroscopic examinations were made by spin-coating of the blends solutions onto spectrosil. The spin-coating speed was adjusted so that thickness of the studied film is ca ~80 nm. The relative Raman cross section of F8BT to that of PFB is calculated as described by Kim et al. [38] utilizing dilute solutions of the homopolymers PFB and F8BT with molecular weight of 62 kg/mol and set of blends with ratios by weight of (80:20), (70:30), (60:40), (50:50) and (40:60). The dilute solutions were prepared through diluting the initial concentration of the solutions to a concentration <0.1% (w/v) to avert probable phase separation in the solutions of the blends. PL efficiency measurements were performed at room temperature in nitrogen purged integrating sphere coupled to an Oriel InstaSpec IV spectrograph. The F8BT:PFB sample were excited using UV line of wavelength 366 nm. The atomic force microscopy (AFM) images were obtained in the tapping-mode configuration using a Nano ScopeIIIa Dimension 3100 (Digital Instruments Inc., Santa Barbara, CA). Fluorescence (PL) microscopy images were captured by (Vickers Photoplan M41) using Hg illumination source such that the samples were studied under either blue or UV light illumination as specified in the text. The UV–vis spectra were measured using Hewlett Packard 8453 UV–Vis spectrophotometer in air with the light beam incident normal to the sample. The Time Correlated Single Photon Counting (TCSPC) room temperature measurements were performed with the sample kept under vacuum of $\sim 10^{-5}$ mbar in a vacuum chamber where the samples were excited by diode laser of wavelengths 407 nm. Photovoltaic device were fabricated in the structure of ITO/PEDOT:PSS/polymer blend/Al using a pre-patterned ITO substrate. First, the ITO substrate was cleaned in ultrasonic bath in Acetone and 2-propanol and oxygen plasma successively for 10 min for each step. Second, a thin layer of poly(3,4ethylenedioxythiophene)polystyrene sulfonic acid (PEDOT:PSS) was spin coated on the substrate and baked at 200 °C for 1 h under N_2 atmosphere. Then the blends solution was spin-coating and subsequently an aluminum (Al) contacts were thermally evaporated onto the film resulting in PV devices of area 4.5 mm^2. The devices were made and then encapsulated in nitrogen filled glovebox. The external quantum efficiency (EQE) of PV devices was measured by illuminating the device through the semi-transparent ITO electrode using a quartz-halogen lamp utilizing a monochromator and measuring the resulted short circuit current by Keithley Instruments 237 source measure unit. A beam splitter was employed to measure the intensity of the light incident on the devices via a calibrated Si photodiode. The Current density–Voltage (*J*–*V*) characteristic of the photovoltaic devices was measured under the illumination of wavelength 400 nm.

The Raman images and spectra of the studied thin film samples were obtained using a WiTec confocal Raman microscope. The samples were excited with helium–neon laser (MellesGriot) of a wavelength 632.8 nm that corresponds to an energy well below the polymers optical bandgap edge so that the photoluminescence

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