

Efficient Charge Photogeneration by the Dissociation of PC₇₀BM Excitons in Polymer / Fullerene Solar Cells

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Supporting Information Placeholder

ABSTRACT: The role of PC₇₀BM excitons in driving charge photogeneration in low bandgap polymer/fullerene bulk heterojunction solar cells has been studied. Both transient absorption spectroscopy (TAS) of charge generation yields in blend films as a function of excitation energies and photocurrent quantum efficiency spectra of the corresponding devices indicate that charge generation in this system results primarily from direct optical excitation of PC₇₀BM. Blend composition studies of photocurrent density and photoluminescence quenching indicate that the efficiency of photocurrent generation is primarily determined by the limited efficiency of PC₇₀BM exciton diffusion to the polymer, due to the formation of PC₇₀BM domains (≥ 5 nm). This limitation becomes more severe as the PC₇₀BM content is increased above 50%. Despite this limitation, and despite the poor charge photogeneration from polymer excitons, organic solar cells fabricated using this photoactive blend layer yielded device photocurrents of 7.1 mA/cm², maximal EQE's of 41% and a device efficiency of 3.1%.

The most efficient organic photovoltaic (OPV) devices are now reaching power conversion efficiencies of 8%.¹⁴ Their active layer consists of a bicontinuous network of a small bandgap polymer and a soluble fullerene that act as an electron donor and acceptor (D/A) pair.⁵ Charge photogeneration in these devices is typically considered to be initiated by photon absorption by the polymer followed by electron transfer from the polymer to the fullerene.^{5,6} However increasing attention is being placed upon the role of the acceptor as an additional light absorbing element of the device, motivated in particular by the increased use of C₇₀ based acceptors such as [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₀BM) which exhibit significant visible light absorption.^{7,8} Charge generation from fullerene excitons can proceed either by direct hole transfer from the fullerene to the polymer (sometimes referred to as reverse electron transfer), or by exciton energy transfer from the fullerene to the polymer followed by the conventional electron transfer from the polymer exciton to the fullerene.^{9,11} Neither of these charge separation pathways have received much attention to date compared to the more conventional charge generation pathway initiated by polymer light absorption in such blend films. Time-resolved spectroscopy experiments have estimated

that hole transfer in polymer/PC₆₀BM films is an ultrafast process with efficiencies limited by phase segregation in the blends.^{9,10,12}

In this letter we report our investigations on the contribution of photoinduced hole transfer to the device photocurrent for an OPV device with an active layer comprising a blend film of the small bandgap polymer BTT-DPP and PC₇₀BM. By means of transient absorption spectroscopy we demonstrate that the BTT-DPP exciton is unable to drive efficient charge separation, with charge photogeneration in the device active layer resulting primarily from PC₇₀BM light absorption, followed by hole transfer from the fullerene to the polymer. Despite the absence of charge photogeneration from polymer excitons, OPV device power conversion efficiencies of 3.1% were achieved. Photoluminescence (PL) quenching experiments, TEM analysis and J/V curves of devices with different composition ratios indicate that diffusion of the PC₇₀BM excitons to the donor/acceptor interface is a key factor limiting this power conversion efficiency. We conclude that optimization of the PC₇₀BM domain size is a key factor influencing the efficiency of BHJ OPV devices employing PC₇₀BM acceptor materials.

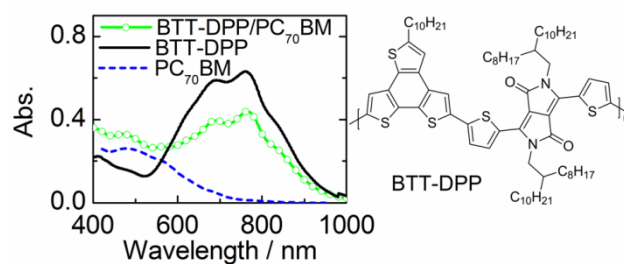


Figure 1. Chemical structure of BTT-DPP and steady state absorption spectra of thin films of BTT-DPP, PC₇₀BM and 1:1 BTT-DPP/PC₇₀BM blend. Films were prepared by spin coating (1500 rpm) solutions with ortho-dichlorobenzene solvent.

The BTT-DPP polymer (Figure 1) was synthesised in a good yield by a microwave-assisted Stille polycondensation between the distannylated benzo[1,2-b:3,4-b':5,6-d''] trithiophene (BTT) unit and the dibrominated 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP) unit.¹³⁻¹⁵ Details of the synthesis, ¹H NMR and

TGA analysis are included in the supporting information (SI). The absorption spectra of thin films of BTT-DPP, PC₇₀BM, and a BTT-DPP/PC₇₀BM blend with a 1:1 weight ratio are plotted in Figure 1. The highest occupied molecular orbital (HOMO) energy level of BTT-DPP was determined by photoelectron spectroscopy in air; a value of -5.20 eV was measured for a thin film spin-cast from chloroform.

Small band gap polymers, such as BTT-DPP, are typically designed to increase the short-circuit current (J_{sc}) of BHJ OPVs by absorbing a larger part of the solar spectrum.^{15,16} However, this shift of the polymer absorption to longer wavelengths typically leads to a decrease in the active layer absorption at shorter wavelengths and increasing interest in the use of blue absorption electron acceptors such as PC₇₀BM. Such acceptor light absorption is particularly important given that typically the active layer of optimised low bandgap OPV devices consists of > 60 weight percent of fullerene.⁷ Low bandgap BHJ devices utilizing PC₇₀BM as an electron acceptor have consistently performed better than the devices with the more common electron acceptor PC₆₀BM.^{7,17-18} Although these two fullerene derivatives have similar ionisation potential (IP), electron affinity (EA) and sizes, the increase in device efficiencies when PC₇₀BM is used has been attributed to its improved light absorption.^{7,19} The increased light absorption of PC₇₀BM relative to PC₆₀BM has been attributed to its lower symmetry resulting in otherwise forbidden singlet transitions in PC₆₀BM becoming allowed.²⁰

We employed transient absorption spectroscopy (TAS) of BTT-DPP/PC₇₀BM blend films to study charge photogeneration as a function of excitation wavelength. Nano- to millisecond TAS has been previously used to monitor the optical absorption of dissociated polarons in thin films of polymer/fullerene blends.^{6,21-24} For the present experiment, excitation pulses were tuned to excite different transitions in the polymer/fullerene blend from 420 nm to 900 nm. In order to keep the measurements as close as possible to the device working conditions under standard AM1.5 illumination, we used excitation densities of $\sim 3 \mu\text{J}/\text{cm}^2$. When excitation intensities could not be precisely adjusted to the desired $3 \mu\text{J}/\text{cm}^2$, the amplitudes of the resulting transient signals were normalized for the different number of absorbed incident photons. In all cases, a broad photoinduced absorption signal was observed across the near-infrared, assigned to BTT-DPP polaron absorption, with data typically being collected at a probe wavelength of 1150 nm, corresponding to the peak of this polaron absorption. All recorded transients showed the same relaxation dynamics (see SI for representative kinetics) independent of the excitation wavelength. These decays fitted well to a single power law ($\Delta\text{OD} \propto t^{-\alpha}$) decay where α (exponent) = 0.8, characteristic of diffusion limited non-geminate recombination of trapped dissociated polarons, as we have reported previously for other polymer:fullerene blend films.^{22,23} The relatively high value of the exponent, α , is indicative of weak charge trapping effects (where $\alpha = 1$ indicates trap-free regime), probably due to relatively shallow trap states. Excitation density dependent measurements of the absorption transients (inset of Figure S3 in the SI) showed a linear dependence over the excitation density range studied. As such, we can conclude that the amplitude of these transient absorption signals (ΔOD) is effectively a relative measure of the external (BTT-DPP*) polaron quantum yield.

Figure 2 presents the ΔOD amplitude measured at 0.2 μs time delay as a function of excitation wavelength. It is apparent that the polaron yield is strongly dependent upon the excitation wavelength. To understand this change in the polaron generation we have also plotted the steady state absorption spectra of the BTT-DPP/PC₇₀BM and PC₇₀BM films. A comparison between the absorption spectra and the transient excitation spectrum reveals that the yield of the polarons is low for polymer excitation, while it increases with the absorption cross section of the PC₇₀BM. Hence, the polaron yield largely follows the PC₇₀BM absorption in the blend film.

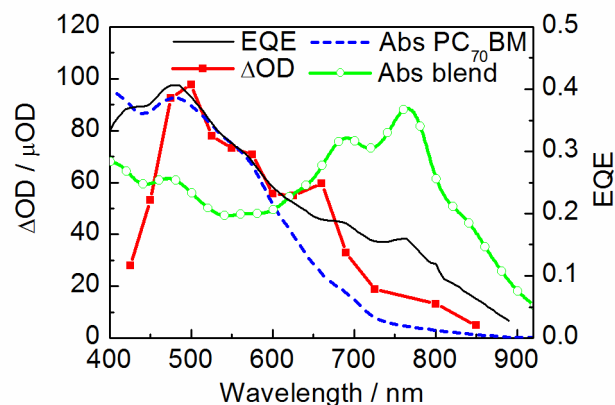


Figure 2. Transient absorption signals (ΔOD) (red-filled squares) at 0.2 μs time delay of a BTT-DPP/PC₇₀BM 1:1 weight ratio thin film plotted as a function of excitation wavelengths. Excitation densities used for TAS were $3 \mu\text{J}/\text{cm}^2$. Probe pulses were set to 1150 nm at the polymer polaron band. TAS data is overlaid with the absorption spectrum of the blend (green open circles) and PC₇₀BM (blue dashed line). The EQE of the corresponding device is plotted as a black line. Data shows that charges in the blend are mainly generated by the dissociation of fullerene excitons.

We turn now to photocurrent generation in BTT-DPP/PC₇₀BM OPV devices. Previously, Clarke et al. have shown that the amplitude of transient absorption signals measured as employed herein for different polymer/fullerene blend films correlates well with the short circuit current of the corresponding OPV devices.²⁵ BTT-DPP/PC₇₀BM solutions with 1:1 weight ratio were spin-coated on an ITO substrate with a layer of PEDOT-PSS and a Ca/Al counter electrode (See SI for details). The external photocurrent quantum efficiency (EQE) spectrum (See Figure 2) measured with this device under monochromatic excitation shows a close correlation with the polaron ΔOD excitation spectrum measured in blend films. Both spectra exhibit the same maximum at ~ 500 nm corresponding to the absorption spectrum of PC₇₀BM in the blend. These photocurrent data confirm that optical excitation of the polymer in the blend does not lead to efficient charge separation. Remarkably, despite photocurrent generation primarily deriving from PC₇₀BM light absorption, the power conversion efficiency of this device was measured under simulated AM1.5 sunlight to be 3.1% (see Figure 3 and SI for details).

The absence of efficient polaron and photocurrent generation following optical excitation of the polymer rules out the possibility that energy transfer from the fullerene to the polymer, followed by LUMO to LUMO electron transfer, contri-

butes to the device photocurrent. This absence of fullerene to polymer energy transfer is consistent with the low oscillator strength for the PC₇₀BM singlet PL, resulting in a low Förster energy transfer rate constant.²⁰ As such, our observation of efficient charge photogeneration in BTT-DPP/PC₇₀BM BHJ devices following PC₇₀BM excitation is assigned to hole transfer from the HOMO level of the fullerene to the HOMO level of the polymer. The greater efficiency of HOMO to HOMO hole transfer compared to LUMO to LUMO electron transfer can be attributed primarily to the material energetics.

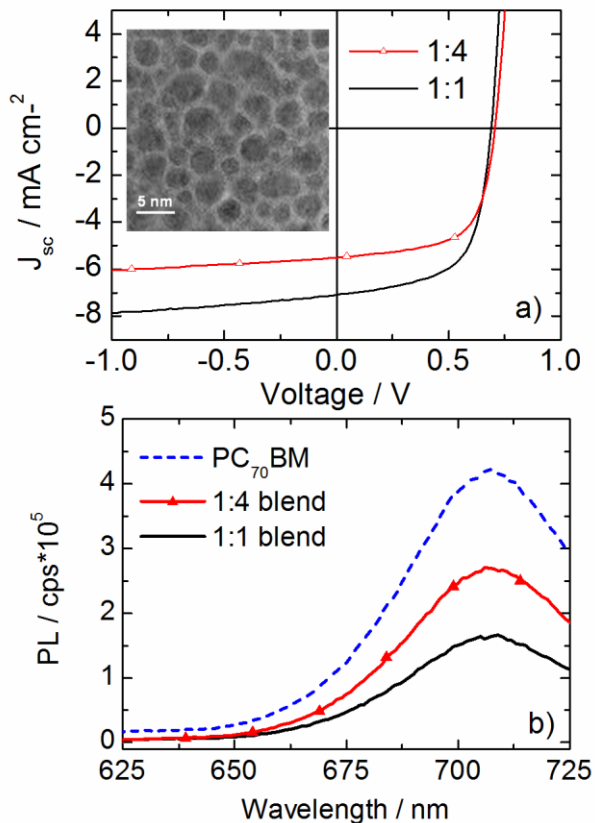


Figure 3. a) J-V curves for BTT-DPP/PC₇₀BM with 1:1 and 1:4 weight ratio blends between -1 and +1 V at 1 sun light intensity. Power conversion efficiencies are 3.1% for 1:1 blend and 2.5% for 1:4 blend. b) Photoluminescence spectra of thin films of PC₇₀BM and BTT-DPP/PC₇₀BM with 1:1 and 1:4 weight ratio. Inset of Figure 3a: A TEM image of approximately 30 nm thick 1:4 weight ratio BTT-DPP:PC₇₀BM thin film stained with iodine showing PC₇₀BM domain formation as the darker areas.

Given our observation of efficient OPV device performance from PC₇₀BM excitons in a 1:1 blend films, we turn now to consideration of devices employing higher PC₇₀BM compositions. BTT-DPP/PC₇₀BM devices with 1:1 and 1:4 weight ratios were prepared; their J/V curves are presented in Figure 3a. Both devices have the same fill factor and open circuit voltage (V_{oc}). However, their J_{sc} differ, with the device with smaller content of PC₇₀BM (7.1 mA/cm²) outperforming that with higher PC₇₀BM content (5.5 mA/cm²). The maximum power conversion efficiencies achieved are 3.1% and 2.5% for 1:1 and 1:4 devices, respectively. We conclude that despite the superior PC₇₀BM light absorption in the 1:4 blend device, the efficiency

of photocurrent generation is lower. In order to investigate the origin of this composition dependence of J_{sc} , we monitored the PC₇₀BM exciton quenching by recording the PL spectra of thin films of PC₇₀BM and 1:1 and 1:4 blend ratios of BTT-DPP/PC₇₀BM, as shown in Figure 3b. The samples were excited at 470 nm, close to the absorption maximum of PC₇₀BM, and monitored the PC₇₀BM emission intensity at \sim 710 nm. There are two striking features of these emission data. First of all it is apparent that the PC₇₀BM emission is more efficiently quenched in the 1:1 blend film compared to the 1:4 blend film. This is consistent with the higher photocurrent density observed for the 1:1 blend device. Secondly it is apparent that even for the 1:1 blend film, the PC₇₀BM emission quenching is relatively modest (\sim 60% relative to the neat PC₇₀BM film). This contrasts to observations of polymer emission quenching observed in most polymer/fullerene BHJ films with adequate LUMO level offsets, which typically exceed 90%. This modest, and composition dependent, PC₇₀BM emission quenching strongly suggests that the efficiency of fullerene exciton diffusion to the charge separation interface is a key factor limiting photocurrent generation in these devices.

We thus conclude that photocurrent generation from PC₇₀BM excitons in these devices is limited by the efficiency of exciton diffusion to the polymer, in agreement with the results from femtosecond transient spectroscopy measurements on MDMO-PPV/PC₆₀BM films by Bakulin et al.⁹ This issue becomes more severe as the PC₇₀BM content of the blend film is increased. This exciton diffusion limitation most probably derives from the tendency of fullerenes to form relatively large, crystalline, domains with sizes larger than their exciton diffusion lengths (\sim 5 nm) in such blend films.^{9,26-30} Indeed, fullerene domain formation has been previously linked to exciton dissociation efficiencies for polymer/PC₆₀BM blends.^{9,12} TEM analysis on thin films of BTT-DPP/PC₇₀BM blends with different composition ratios confirmed the presence of a range of PC₇₀BM rich domain sizes in blends with high PC₇₀BM concentrations (inset of Figure 3a). Further data from the TEM measurements are included in SI. We note that it is likely that the blend films analyzed herein are likely to comprise both intimately mixed polymer/fullerene regions as well as relatively pure domains.²⁷ As such the photocurrent reported herein may derive primarily from PC₇₀BM located in the mixed domains. In any case, these results suggest that a key consideration for the optimization of OPV devices where PC₇₀BM excitons contribute significantly to photocurrent will be control of PC₇₀BM domain size, and in particular the avoidance of the formation of pure PC₇₀BM domains with diameters greater than 5-10 nm. To quantify the potential gain achieved from this strategy, we note that the 1:4 blend film reported herein exhibits a PC₇₀BM photoluminescence quenching efficiency of only 35%. If this could be increased to 90% (typical for polymer PL quenching in such films), we estimate the device photocurrent deriving from PC₇₀BM absorption alone would increase to 14.1 mA/cm², resulting in a potential device efficiency, without including photocurrent generation from the polymer, of $>$ 6%.

In conclusion, we have used transient absorption spectroscopy to study the charge photogeneration in BTT-DPP/PC₇₀BM BHJ blends. The results from TAS and device characterization data reveal that light absorption by PC₇₀BM and not by the polymer is the main contributor to the device photocurrent.

Charge separation is mediated by hole transfer from the fullerene HOMO level to the polymer HOMO level. Electron transfer from the polymer LUMO to the PC₇₀BM LUMO is suppressed probably due to a smaller driving force for charge separation. Evidence is provided that charge photogeneration from direct hole transfer from the PC₇₀BM to the polymer can produce significant device photocurrents. It is thus not surprising that typically BHJ OPVs with a polymer/PC₇₀BM active layer show improved performance than the OPVs with polymer/PC₆₀BM active layers.^{7,17,18} By controlling the BTT-DPP/PC₇₀BM composition ratio we were able to optimise the device power conversion efficiencies to a maximum of 3.1%. In addition, we have shown that device J_{SC} is limited by the efficiency of the PC₇₀BM exciton dissociation, attributed to the tendency of PCBM to form large, relatively pure domains with domain sizes longer than the PCBM exciton diffusion length.

ASSOCIATED CONTENT

Supporting Information. Synthesis of monomers and the copolymer, ¹H NMR and TGA analysis. Experimental details for device preparation and transient absorption spectroscopy. Transient decays of a BTT-DPP/PC₇₀BM film and excitation density dependent TAS, This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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ABBREVIATIONS

TAS, transient absorption spectroscopy; OPV, organic photovoltaic; ΔOD, change in the optical density; BHJ, bulk heterojunction; J_{SC}, short circuit current; IP, ionization potential; EA, electron affinity; D/A, donor/acceptor; BTT, benzo[1,2-b:3,4-b':5,6-d''] trithiophene; DPP, 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione; EQE, external quantum efficiency; PL, photoluminescence; TEM, transmission electron microscopy.

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