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Towards Optimisation of Photocurrent from Fullerene Excitons in Organic Solar Cells

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Photocurrent from fullerene excitons in polymer/fullerene solar cells is optimised by employing a series of low bandgap diketopyrrolopyrrole-containing polymers with differing molecular weights. The low LUMO level of this donor polymer prevents efficient charge generation from polymer excitons, allowing us to focus on charge and photocurrent generation specifically from fullerene excitons. We employ femtosecond transient absorption spectroscopy and transmission electron microscopy to show a correlation between fullerene domain size and the kinetics of polaron generation from fullerene excitons, and relate these observations to device efficiency. Charge generation from fullerene excitons is shown to occur on the 0.5 ns timescale, limited by the kinetics of diffusion of fullerene excitons to domain interfaces with donor polymers. For devices employing the highest molecular weight donor polymer, ~ 7 mA.cm⁻² of photocurrent is observed from fullerene excitons, leading to an overall device efficiency of 5.2 %.

Introduction

Polymer/fullerene organic solar cells (OSC) have the potential to provide an inexpensive and efficient solar technology.¹ They consist of a film of a photoactive electron-rich polymer and electron-poor fullerene sandwiched between two electrodes. In the film, both the polymer and fullerene absorb sunlight and their excitons generate charges via a series of charge transfer steps driven by the energy differences of the polymer and fullerene frontier molecular orbitals.^{2,3} Research efforts have in recent years been particularly focused on developing new donor polymers for more efficient light harvesting and charge photogeneration.⁴⁻⁶ With the development of these lower bandgap polymers, the role of the fullerene in absorbing higher energy photons has become increasingly important, leading to increasing use of the asymmetric, fullerene, PC₇₀BM due to its high absorption coefficient.⁷ However, relatively few studies have focused on investigating and optimising the generation of photocurrent resulting from this fullerene light absorption.⁸⁻¹² Such photocurrent generation can be assigned to dissociation of fullerene excitons at polymer/fullerene interfaces, corresponding to a HOMO to HOMO hole transfer reaction.^{9,10,13}

Several studies have considered the importance of fullerene aggregation within the blend film in relation to device performance.^{12,14-17} It has been suggested that fullerene aggregation may be important in stabilising charge separation and providing more efficient charge transport and collection at the electrodes.¹⁸ Conversely, we and others have identified that fullerene aggregation into domains with diameters bigger than their exciton diffusion length can limit device photocurrents due to inefficient exciton diffusion to the polymer/fullerene

interface.^{8-10,13}

In this paper, we focus on the kinetics of fullerene exciton diffusion and charge separation, employing blend films of PC₇₀BM with the donor polymer BTT-DPP (see **Figure 1** for polymer's structure). We have previously shown that photocurrent generation in OSC employing these photoactive layer materials primarily results from fullerene light absorption,¹³ with BTT-DPP excitons being too low in energy to drive efficient charge separation.¹⁹ Herein, we employ a series of BTT-DPP fractions with differing molecular weights in order to optimise film microstructure and to investigate the correlation between fullerene singlet exciton dynamics and photocurrent generation. Following this approach we are able to achieve ~ 7.3 mA.cm⁻² photocurrents from PC₇₀BM excitons alone. We furthermore demonstrate that this impressive photocurrent generation is limited by fullerene exciton dissociation in these devices primarily occurring with a 0.5 ns time constant. Optimised devices reached power conversion efficiencies (PCE) of 5.2%, with device photocurrents resulting primarily from fullerene light absorption.

Results and Discussion

In the devices employed herein, the primary function of the donor BTT-DPP polymer is as a hole transport material, with the PC₇₀BM playing the role of electron transport material and primary light absorber for photocurrent generation. Previously, we have shown that photocurrents from BTT-DPP:PC₇₀BM devices are largely limited by the poor microstructure of the active layer.¹³ To optimise this microstructure, we synthesised BTT-DPP and subsequently fractionated it to yield three BTT-

DPP fractions with number average molecular weights (M_n) of 22 (BTT-DPP-22), 73 (BTT-DPP-73) and 90 (BTT-DPP-90) kg.mol⁻¹.^{20,21} Bulk heterojunction solar cells were fabricated with a standard ITO/PEDOT:PSS/polymer:PC₇₀BM/Ca/Al structure. For all three BTT-DPP fractions, a 1:2 weight ratio (polymer:fullerene) blend composition was found to give optimum device efficiency. **Figure 1a** shows the J/V characteristics of BTT-DPP-22/PC₇₀BM, BTT-DPP-73/PC₇₀BM and BTT-DPP-90/PC₇₀BM devices under simulated 1 sun (AM1.5) irradiation, with the corresponding performance data being listed in **Table 1**. The differences in J_{SC} between these devices should be highlighted. The BTT-DPP-90 based device has ~3.5 times higher photocurrents than the BTT-DPP-22 based device, which can only be partly explained by differences in film thickness (see the supporting information (SI)). However, the open circuit voltage (V_{OC}) and fill factor (FF) of all devices were found to be rather invariant. Therefore, the BTT-DPP-90 based device had a maximum average PCE of 5.2%, whereas the BTT-DPP-73 and BTT-DPP-22 based devices had only 2.8% and 1.5%, respectively. It is also notable that, given these devices were fabricated without any processing additives or annealing steps, their FFs are remarkably high, up to 0.72, indicating that charge collection in these devices is remarkably efficient, as we investigate further below.

Figure 1. J/V curves (a) and EQE spectra (b) recorded under simulated 1-sun AM1.5 illumination for BTT-DPP-22/PC₇₀BM (22), BTT-DPP-73/PC₇₀BM (73) and BTT-DPP-90/PC₇₀BM (90) devices (1:2 wt. ratio).

For the EQE measurements, cells were kept under constant 1-sun illumination and then exposed to weak monochromatic light.

The external quantum efficiency (EQE) spectra shown in **Figure 1b** primarily track the PC₇₀BM absorption spectrum, with only minor contributions from BTT-DPP absorption in the near infrared, as we have discussed previously.¹³ We estimate that by de-convoluting the EQE spectra with the polymer and fullerene absorption spectra (shown in the SI) the PC₇₀BM light absorption yields on average 70±15% of the overall photocurrent generation in the most efficient devices (BTT-DPP-90/PC₇₀BM). This leads to photocurrent densities from fullerene excitons alone reaching ~7.3 mA.cm⁻² for the BTT-DPP-90 device.

In order to investigate this trend in photocurrent generation, we carried out femtosecond transient absorption (TA) spectroscopy of thin films of the three different molecular weight blends, as well as neat polymer and fullerene control films.²² Blends were excited at 470 nm (primarily fullerene absorption) and 800 nm (polymer absorption). The neat fullerene and polymer films were excited at 470 and 800 nm, respectively. In **Figure 2a**, we compare the TA spectra of the neat BTT-DPP-90 and BTT-DPP-90/PC₇₀BM blend films recorded at 0.25 ps and 6.2 ns delay times, whilst **Figures 2b** and **2c** show transient kinetics at selected probe wavelengths.

We consider first the neat film data. No detectable signals (< 3×10⁻⁵ OD) were observed from the neat fullerene film under the relatively low excitation densities employed (7.5 μJ.cm⁻²), suggesting that any photoinduced fullerene species exhibit low extinction coefficients relative to polymer excitons/polarons. In contrast, the neat polymer film exhibited a broad positive signal (Figure 2a) assigned to photoinduced absorption of singlet excitons, which was observed to decay mono-exponentially with a 15 ps time constant (Figure 2b). This polymer singlet exciton absorption increases monotonically between 1000 and 1400 nm, and can be readily distinguished from that of BTT-DPP positive polarons which exhibit an absorption maximum at 1200 nm.¹⁹

The blend film showed a more complex TA spectral evolution, as shown in Figure 2a. For both 470 and 800 nm excitation, the initial (0.25 ps) photoinduced absorption spectrum resembles that of the neat polymer and is therefore assigned to polymer excitons (note that BTT-DPP also absorbs weakly at 470 nm). At later times (6.2 ns) the transient spectra take the shape of BTT-DPP polarons and this is therefore assigned to charge-separated polarons. However, the relative magnitudes of these signals and their temporal evolution depend strongly upon the excitation wavelength (Figures 2a and 2b) and polymer molecular weight (Figure 2c).

Figure 2b displays representative transients for the neat BTT-DPP-90 film and blend recorded at 1200 nm for a 470 nm (fullerene) and 800 nm (polymer) excitation. It is apparent that, following the 800 nm excitation, the transient kinetics are dominated by the circa 15 ps decay also observed for neat BTT-DPP assigned to polymer singlet exciton decay to ground state, with only a relatively small residual long-lived signal deriving from BTT-DPP polarons. This is consistent with our previous observations of relatively inefficient charge generation from BTT-DPP excitons.^{13,19} In contrast, excitation at 470 nm results in a pronounced, relatively slow (~0.5 ns) rise in BTT-DPP polaron signal, indicative of BTT-DPP polaron formation from fullerene singlet excitons.²³ The large amplitude of this absorption rise (see also Figure 2a) is consistent with our device

EQE spectra (Figure 1b) indicating relatively efficient charge generation from PC₇₀BM excitons, and in agreement with our previous, microsecond timescale, transient studies.¹³ The slow timescale of this rather efficient charge separation (~ 0.5 ns) is in marked contrast to the ultrafast (sub-picosecond) charge separation typically observed from most polymer excitons,^{24,25} although examples of slow charge separation from polymer excitons has also been previously observed.²⁶ It is striking that charge separation from PC₇₀BM excitons is so slow, due to diffusion limitations (~ 0.5 ns), but still relatively efficient.

Figure 2. (a) TA spectra of the BTT-DPP-90/PC₇₀BM blend for a 470 and 800 nm excitation recorded at 0.2 ps and 6.2 ns after light absorption. The neat polymer spectrum at 0.25 ps is

included as a reference. (b) The corresponding TA kinetics of the BTT-DPP-90/PC₇₀BM blend and neat polymer measured at 1200 nm. (c) As for (b) but comparing blends with the different M_n polymers following 470 nm, excitation. Data in (b) and (c) were normalized at 0.25 ps.

We now focus on comparing the charge photogeneration properties of the PC₇₀BM excitons in the three different molecular weight (M_n) BTT-DPP/PC₇₀BM blends. It is apparent from the absorption rises shown in Figure 2c that PC₇₀BM excitons generate polarons faster and more efficiently in blends with higher molecular weight BTT-DPP. This enhancement of charge photogeneration follows the same trend as the J_{SC} in Figure 1a, and is in line with our observation that PC₇₀BM excitons are the main contributors to device photocurrents. We note that the only difference between these devices is the molecular weight of the polymer and therefore the most likely cause of this improvement of charge photogeneration is optimisation of the morphology of the films. To verify this hypothesis, we carried out TEM and wide angle X-ray scattering (WAXS) measurements of blend films. TEM micrographs (Figure 3) clearly show a coarser domain structure (>5 nm domains) and higher crystallinity for the BTT-DPP-22/PC₇₀BM film relative to BTT-DPP-90/PC₇₀BM. Similarly, WAXS measurements (Figure S3 in the SI) indicate that the crystallinity in these blends increases in the order $90 < 73 < 22$. It is thus apparent that fractionation of BTT-DPP has a significant impact on the morphology of the active layer, decreasing film crystallinity and domain size with increasing polymer M_n .

Figure 3: TEM images (bright field) of thin films of 1:2 weight ratio BTT-DPP-22/PC₇₀BM (a) and BTT-DPP-90/PC₇₀BM (b)

blend films. Dark grey patches correspond to PC₇₀BM-rich domains. (c) Diagram depicting the exciton diffusion process within fullerene aggregates with different diameters. We note that this diagram does not represent realistic film morphology of the studied films, in which the presence of mixed polymer-fullerene phases is likely.

Previous studies have reported fullerene singlet exciton diffusion lengths of 5 nm, of similar order of magnitude to the domain sizes apparent in our TEM images.²⁷ In order to investigate this further, we used steady-state photoluminescence (PL) spectroscopy and time-correlated single photon counting to estimate the fullerene singlet excitons and lifetimes in the blends studied herein. The results of these measurements are included in Table 1. They reveal that indeed fullerene singlet excitons are quenched more efficiently and their lifetime is shorter in the more amorphous BTT-DPP/PC₇₀BM films. We observe a relatively good match between the PL lifetimes and the corresponding charge photogeneration time constants determined from the TA data. Our observed correlation between PL, TEM and TA spectroscopy provides strong evidence that charge photogeneration from fullerene excitons is primarily diffusion limited due to fullerene aggregation on the length scale of the fullerene singlet exciton diffusion length.

M _n kg/mol	V _{oc} V	J _{sc} mA/cm ²	FF	PCE %	τ _{rise} ns	τ _{PL} ns	PLQ
90	0.68	10.5	0.72	5.2	0.52	0.45	0.50
73	0.69	5.7	0.70	2.8	0.68	0.50	0.47
22	0.70	2.9	0.69	1.4	~	0.53	0.32

Table 1. The table presents polymer molecular weights, device J/V characteristics, the rise-time (τ_{rise}) of the TA (obtained by non-linear least square fitting of the kinetics shown in Figure 2c with two exponential functions convolved with a Gaussian function representing the experimental response function), PCBM photoluminescence lifetime (τ_{PL}) and steady state quenching (PLQ). Photoluminescence data is included in the SI. The PL lifetimes (τ_{PL}) were calculated from the average of a two-exponential decay fit to the PL decays. M_n is a number average molecular weight. Error bars of τ_{rise} and τ_{PL}: ±0.1 ns.

The ability of PC₇₀BM singlet excitons to drive reasonably efficient charge separation on relatively long (0.5 ns) timescales can be understood from its relatively long singlet exciton lifetime. The PL decay of neat PC₇₀BM was observed to be 0.65 ns,²⁸ indicative of the relatively slow decay of fullerenes singlet excitons compared to many donor polymer excitons (c.f.: 15 ps for the BTT-DPP singlet excitons observed herein).^{23,29-31} The efficiency of fullerene exciton dissociation can be estimated from the steady state PL data to range from ~50 % for the BTT-DPP-90/PC₇₀BM blend to 30 % for BTT-DPP-22/PC₇₀BM, suggesting that for all the films studied, fullerene exciton decay prior to charge separation remains a significant loss pathway. We note that similar PCBM exciton quenching has been observed for other donor polymers,^{8,17,23} suggesting that our conclusion of significant losses associated with fullerene exciton diffusion limitations may be an important loss factor for many polymer/fullerene solar cells.

Optical excitation of neat fullerene films has been reported to result in direct generation of separated charges, albeit with modest quantum efficiencies.³²⁻³⁴ Whilst the data reported herein can not rule out low yields of charge generation within PCBM domains, our observation of similar kinetics for both PCBM

exciton decay and polymer polaron generation, and similar dependencies upon domain size, indicate that the primary charge generation mechanism in the system studied herein is exciton diffusion to, and charge separation at, the PCBM/polymer interface.

Figure 4. (a) Transient photovoltage and photocurrents. Inset: calculated non-geminate recombination flux J_{LOSS} with voltage bias for different light intensities 0.5, 1 and 2 suns (lines are mono-exponential fits). (b) Reconstruction of the current density of BTT-DPP-90/PC₇₀BM device in the fourth quadrant and different light levels ranging from 0.5 to 2 suns.^[19] Symbols are experimental data and full lines are reconstructed data.

We turn now to consideration of charge collection in these devices, and particularly our observation of very high FFs and invariable V_{OC}. To address this, we recorded the J_{SC} versus light intensity response of a representative BTT-DPP-90/PC₇₀BM device from 0 to 4 suns (device FF and V_{OC} did not vary significantly between blends, suggesting that device energetics and charge transport properties were invariant with polymer M_n). The result presented in the SI Figure S4 reveals a remarkably linear response of J_{SC} with light intensity (J_{SC} proportional to I^{0.97}) even at 4 suns, indicative of highly efficient charge collection and relatively low non-linear recombination losses at short-circuit in these devices. Furthermore, we used charge extraction and transient photovoltage/photocurrent techniques to quantify charge densities and charge lifetimes in the active layer as a function of voltage and light bias.³⁵ Typical photocurrent and photovoltage transients are shown in Figure 4a, showing decay times of 1*10⁻⁷ and 5.1*10⁻⁶ s respectively, with the substantially faster decay time at short circuit being consistent with efficient charge collection. Such transients were employed in the successful reconstruction of the experimental device J/V curves (Figure 4b)

and photovoltages (Figure S5 in the SI) in the fourth quadrant for a wide range of illuminations, employing as previously a model that assumes that non-geminate recombination of charges is the only voltage dependent photocurrent loss pathway in the device.³⁶

The observed excellent match of recreated and experimentally observed J/Vs, apparent in Figure 4b, confirms that non-geminate recombination governs the BTT-DPP/PC₇₀BM device FF and V_{OC}. The non-geminate recombination flux (Figure 4a, insert) only becomes significant (> 1 mA.cm⁻²) for voltages greater than 0.57 V, approaching V_{OC} and consistent with the high device FFs.

The efficient charge collection observed for the devices studied herein, and resultant high device fill factors, can be understood in terms of the kinetics of charge extraction relative to non-geminate recombination. Using charge extraction at short circuit, we estimated that indeed the effective transverse carrier mobility in the BTT-DPP-90/PC₇₀BM device is $\sim 2 \times 10^{-4}$ cm².V⁻¹.s⁻¹, comparable to P3HT.³⁷ Despite these relatively high charge carrier mobilities, the charge carrier lifetimes are reasonably long, being $\sim 4 \times 10^{-6}$ s for charge densities of 2×10^{16} cm⁻³ at open-circuit condition, again comparable to P3HT devices, and indicative of a film micro- or interface structure which reduces recombination losses and thereby favors efficient charge collection.³⁸

Conclusions

In summary, we have demonstrated the design and characterization of BTT-DPP/PC₇₀BM photovoltaic devices in which the fullerene excitons alone generate impressive > 7.3 mA.cm⁻² photocurrents. The low bandgap polymer BTT-DPP was synthesised and fractionated into three different molecular weights to optimise the morphology of the films for more efficient charge photogeneration from PC₇₀BM excitons. As a result of this, device J_{SC} increased with polymer molecular weight. The most efficient device prepared with the highest molecular weight polymer showed an impressive FF of 0.72 and PCE of 5.2%. The high FF results from slow non-geminate recombination losses relative to charge extraction, indicative of a favourable film microstructure for efficient charge collection. Using PL and femtosecond TA spectroscopy, we find that charge generation from PC₇₀BM excitons occurs primarily on the ~ 0.5 ns timescale. The higher efficiency, relatively slower, charge generation from fullerene excitons compared to that from BTT-DPP excitons is enabled by the slower intrinsic decay time of fullerene singlet excitons (0.65 ns compared to 15 ps for BTT-DPP excitons), as well as by the more favourable energetics for hole rather than electron transfer. The efficiency of PC₇₀BM exciton driven charge separation is observed to be dependent upon polymer molecular weight, assigned to variations in the PC₇₀BM domain size on the length scale of the PC₇₀BM singlet exciton diffusion length. Our results demonstrate that efficient photocurrent generation in polymer/fullerene OSCs can be achieved even with relatively slow exciton-diffusion-limited charge separation kinetics. They also emphasize that light absorption by fullerenes can result in high photocurrents, with the efficiency of this process being dependent in particular upon the efficiency of fullerene exciton diffusion to the charge separation interface, and therefore dependent upon fullerene domain size.

Experimental

Device preparation

Optimized devices were fabricated with the fractionated BTT-DPP polymers co-dissolved with PC₇₀BM (Solenne BV) in a chloroform/o-dichlorobenzene (4:1) mixed solvent with a weight ratio of 1:2 and a 25 mg/ml concentration. ITO substrates with sheet resistance 15 Ω sq⁻¹ (PsioTec Ltd, UK) were sonicated in detergent, acetone and isopropanol sequentially and then treated in an oxygen plasma asher (100 W, 7 min). PEDOT:PSS was spin-coated over the ITO substrates at 3500 rpm and baked on a hot plate at 150°C in air for 20 min. The BTT-DPP/PC₇₀BM solutions were spin-coated onto the PEDOT:PSS layer at the optimum for this blend 3000 rpm in air and transferred to a nitrogen glove box (<10 ppm O₂, H₂O), where Ca/Al (25 nm/100 nm) electrodes were deposited by thermal evaporation under vacuum. Device area was 0.045 cm².

Device and film characterisation

J/V curves were measured with a 150W xenon arc lamp filtered to simulate AM1.5 conditions (LOT Oriel) and a Keithley 238 source measure unit. EQE spectra were measured using a 100 W Tungsten-Halogen lamp. The photocurrent was measured using a Keithley 2400 source meter. A calibrated silicon photodiode with appropriate long pass filters was used as a reference in the J/V and EQE measurements.

PL spectra were measured with a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) with a 470 nm monochromatic excitation. PL dynamics were recorded using Time-Correlated Single Photon Counting, employing a Horiba Jobin Yvon IBH Fluorocube system. Excitation was 467 nm, 1 MHz repetition rate and 80 μ W.cm⁻². Decays were recorded at 700 nm, the maximum PC₇₀BM PL.

Femtosecond transient absorption spectroscopy

Thin films of BTT-DPP-22/PB₇₀BM, BTT-DPP-73/PB₇₀BM and BTT-DPP-90/PB₇₀BM blends were prepared on a glass substrate following the same procedure used during device fabrication. Samples were excited with 470 nm and 800 nm ~ 7.5 μ J.cm⁻² pulses, generated by a commercially available optical parametric amplifier TOPAS (Light conversion) pumped by a Solstice Ti:Sapphire regenerative amplifier (Newport Ltd). Changes in the optical density of the films induced by the laser excitation were followed with a second broadband pulse (830-1450 nm) generated in a sapphire crystal. HELIOS (Ultrafast systems) transient absorption spectrometer was used for recording the dynamics of the transient absorption spectra up to 6.5 ns with average 200 fs IRF.

Wide angle X-ray scattering (WAXS)

Samples for WAXS measurements were prepared in a drop-casting manner with the solutions used for device fabrication. The measurements were carried out with a Panalytical X'Pert-Pro MRD which has a nickel-filter Cu K α 1 beam and an X'Celerator detector, using a current of 40 mA and an accelerating voltage of 40kV.

Transmission electron microscopy

For TEM examination, BTT-DPP solutions were spun onto

PEDOT:PSS-coated (10 nm) glass substrates, retrieved on holey carbon films. The sample film thickness was ~30 nm. The samples were then stained by RuO₄ vapour to increase the contrast of fullerene and polymer domains and measured with Titan 80/300 transmission electron microscope.

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Notes and references

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Towards Optimisation of Photocurrent from Fullerene Excitons in Organic Solar Cells

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Supporting information

10 Figure S1. GPC traces for the BTT-DPP fractions with number average molecular weights 22 (BTT-DPP-22), 73 (BTT-DPP-73) and 90 (BTT-DPP-90).

Figure S2: a) Steady-state absorption spectra of thin films of the neat BTT-DPP-90, BTT-DPP-73, BTT-DPP-22 and PC₇₀BM films. Experimentally determined EQE spectra of BTT-DPP-90/PC₇₀BM, BTT-DPP-73/PC₇₀BM and BTT-DPP-22/PC₇₀BM devices are plotted in b), c) and d), respectively. Non-linear least square fits of the EQE spectra and de-convoluted spectral contributions of PC₇₀BM and the polymers are also included in the graphs. The spectral contributions of PC₇₀BM and BTT-DPP-polymers were received by non-linear least-square fitting of their corresponding EQE spectra with the steady-state absorption spectra of the polymer and fullerene shown on Figure S2a. Error bars of the fits were 15% (b), 10% (c), 10% (d). We note that the absorption spectra used in these fits were measured on films and the corresponding fits do not take into account interference effects due to the presence of electrodes.

Figure S3: Wide angle X-ray scattering patterns of drop-casted films of fractionated BTT-DPP/PC₇₀BM blend films on Si/SiO₂ substrates. Polymer lamellar and PC₇₀BM stacking peaks are marked with arrows. The increase in amplitude and decrease in FWHM of these peaks show that order in the films is increasing.

M _n [kg.mol ⁻¹]	M _w [kg.mol ⁻¹]	Film thick. [nm]
90	188	100
73	155	80
22	34	50

Table S1. The table presents polymer molecular weights and thicknesses of the films as measured with a Veeco Dektak profilometer. M_w is the weight average molecular weight of the polymer. M_n is the number average molecular weight. Our previous estimates of device J_{SC} for many different systems (using the matrix-modelling technique under the assumption of 100 % IQE) as a function of thickness show that the observed here almost 4-fold increase in J_{SC} from BTT-DPP-22/PC₇₀BM to BTT-DPP-90/PC₇₀BM device (see Figure 1 and Table 1 in the main text) have origin other than changes in device thickness as confirmed by our TAS analysis.

Figure S4: BTT-DPP-90/ PC_{70}BM device J_{SC} vs. light intensity. The arrows point out the result of power law fits over different range of illuminations.

Figure S5: Prediction of the photovoltage based on measurements of charge density at open-circuit and carrier lifetime for the illumination range 1%- 600% of one sun for the BTT-DPP-90/ PC_{70}BM device.

Figure S6: Lifetime of total charge carriers at different charge densities measured using charge extraction at open-circuit and transient photovoltage for the BTT-DPP-90:PC₇₀BM device.

Figure S7: Photoluminescence spectra (a) and decays (b) of BTT-DPP-90:PC₇₀BM, BTT-DPP-73:PC₇₀BM, BTT-DPP-22:PC₇₀BM blends and neat PC₇₀BM films. Decays were acquired using TCSPC technique with a 200 ps instrument response function. The excitation wavelengths for both experiments were 470 and 467 nm.

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TOC

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Broader context paragraph

The sun is our most sustainable energy source and can be effectively used for an off-grid and on-grid power supply. However, current solar cell technologies still do not provide low cost power to be able to compete with fossil fuels. A particularly popular approach to reducing the cost of solar cells, gaining a high momentum in the past 10 years, is the use of organic materials as the photoactive component. Such organic solar cells can be fabricated to be light-weight, thin and flexible, thus making them ideal for off-grid applications and building integration. Polymer/fullerene solar cells are a type of organic solar cells that are now reaching 10% power conversion efficiency. In these solar cells, polymers and fullerenes absorb sunlight and generate photocurrent, but the way they do that and what limits their photocurrent generation properties is still currently widely debated and as a result difficult to control. In this paper, we explore the limitations of photocurrent generation from fullerene excitons. We apply time-resolved laser spectroscopy and opto-electronic experimental techniques to show that fullerene aggregation is the main cause for reduced photocurrent generation from fullerene excitons. We show that by careful control over polymer molecular weight, the photocurrent from fullerene excitons can be optimised to give solar cell devices reaching 5% efficiency.