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Triplet Formation in Fullerene Multi-Adduct Blends for Organic Solar Cells and Its Influence on Device Performance

By Clare Dyer-Smith, Luke X. Reynolds, Annalisa Bruno, Donal D. C. Bradley, Saif A. Haque,* and Jenny Nelson*

In organic solar cells, high open circuit voltages may be obtained by choosing materials with a high offset between the donor highest occupied molecular orbital (HOMO) and acceptor lowest unoccupied molecular orbital (LUMO). However, increasing this energy offset can also lead to photophysical processes that compete with charge separation. In this paper the formation of triplet states is addressed in blends of polyfluorene polymers with a series of PCBM multi-adducts. Specifically, it is demonstrated that the formation of such triplets occurs when the offset energy between donor ionization potential and acceptor electron affinity is ~ 1.6 eV or greater. Spectroscopic measurements support a mechanism of resonance energy transfer for triplet formation, influenced by the energy levels of the materials, but also demonstrate that the competition between processes at the donor–acceptor interface is strongly influenced by morphology.

Charge separation is understood to occur as a result of the following steps: the formation of the singlet exciton by light absorption is followed by transfer to a geminate pair, also known as a charge-transfer state, where the charges are Coulombically bound to one another. If the charges are able to escape their mutual Coulombic attraction to form separate polarons, they can be collected at the electrodes. There are also a number of undesirable processes that can lead to energy losses, resulting in incomplete conversion of absorbed light to electrical power: the polarons can recombine bimolecularly before reaching the electrodes; the geminate pair can recombine, either by nonradiative relaxation to the ground state, regeneration of the singlet exciton to give delayed photoluminescence (PL), or by luminescence directly from the charge transfer state (so-called exciplex emission^[2,10–13]). In addition, triplets can be formed from intersystem crossing of the exciton, or by intersystem crossing of the charge separated state followed by charge recombination.^[3,9,14] Figure 1 summarizes these processes.

1. Introduction

Organic solar cells are a promising technology with the potential to produce large-area devices at low cost. The efficiency of charge separation at the interface between donor and acceptor domains is a key determinant of photocurrent generation in such devices.^[1] Several recent studies have outlined the importance of interfacial excited states in the performance of solar cells, and the dynamics of processes at the donor–acceptor interface is of crucial importance in determining charge photo-generation yield.^[2–9]

Although some attempts have been made^[15,16] to harness the long lifetime of the triplet state to improve charge separation efficiency (by increasing the exciton diffusion length), it is also understood that triplet states in organic materials may be undesirable due to their greater reactivity (for example with the triplet ground state of oxygen molecules), or to the fact that they may act as an energy trap, and hence as a pathway to exciton loss. This is particularly the case when the energy of the triplet is lower than the energy of the charge separated state, presenting an additional energy barrier to charge separation.^[17]

In many donor–acceptor blends, the energy offset between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor has been correlated with the open-circuit voltage of the device,^[18,19] and is understood to represent the energy of the charge separated state that is a precursor to fully separated charges. This implies that an increase in the open circuit voltage can be achieved by choosing materials that lead to a high charge-separated state energy. In blends with the commonly used electron acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester

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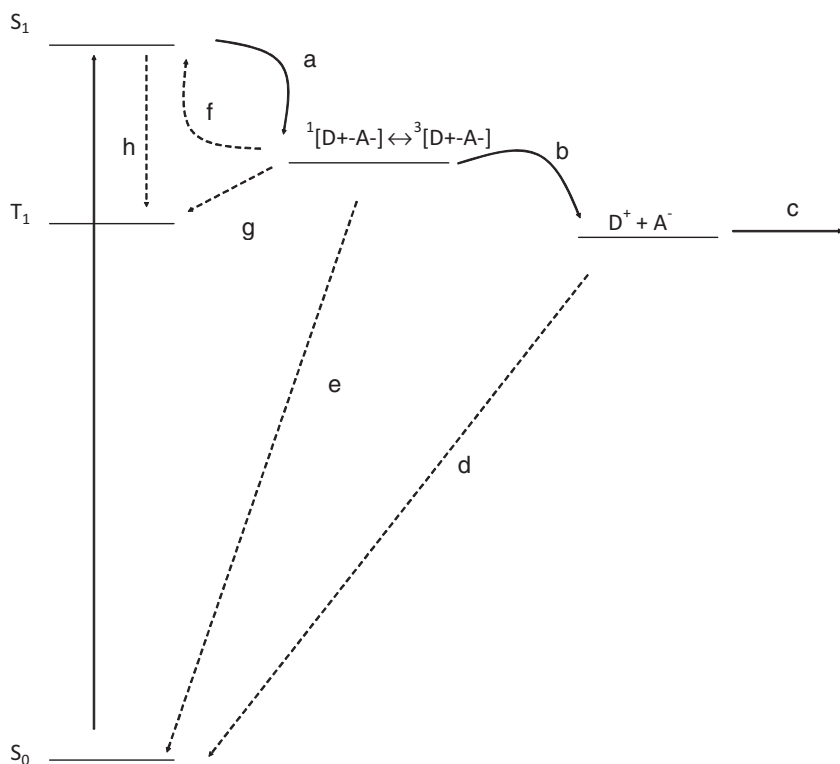


Figure 1. Illustration of key processes in charge separation: a) conversion of singlet exciton to charge-transfer state, b) separation of charge-transfer state to give polarons, c) transport of charges to electrodes, d) bimolecular recombination, e) geminate recombination to ground state (may result in exciplex emission), f) geminate recombination to singlet exciton, g) geminate recombination to triplet, h) intersystem crossing.

(PCBM) this is achieved through the use of high ionization potential (IP) polymers, which have the additional advantage of being more resistant to oxidative degradation by virtue of their deep HOMO level.

However, increasing the charge separated state energy (by increasing the HOMO–LUMO offset) can lead to the formation of other excited states in competition with charge separation if the energy of the charge separated state is higher than these other excited states. In particular, triplet formation has been identified as a major loss of short circuit current density (J_{sc}) relative to calculated values,^[8] and we wish to address the question of how large the HOMO–LUMO offset energy can be before triplet formation begins to compete with charge separation. We measure the formation of triplets using transient absorption spectroscopy, and compare this to photocurrent generation by measurements on photovoltaic devices.

In this paper we define the quantity ΔE_{cs} as the difference between the ionization potential of the donor (IP_D) and the electron affinity of the acceptor (EA_A), where IP_D and EA_A are obtained from cyclic voltammetry measurements in solution. Veldman et al. recently performed detailed studies^[8] on a range of donor and acceptor materials and arrived at a general expression for the charge transfer state energy E_{CT} for a range of materials, using only the oxidation and reduction potentials acquired from cyclic voltammetry, and the optical

bandgap. A constant correction term of 0.29 ± 0.02 eV was included and was determined from measurements of emissive charge transfer states (also known as exciplexes) to account for binding energies that it is not possible to measure directly. In the present work, the definition of ΔE_{cs} does not include this correction term, as we are interested in a trend in behaviour across a series of materials with predictive power for future material combinations. The use of an empirically determined value of ΔE_{cs} without this constant correction will not affect our conclusions.

The donors poly(9,9-dioctylfluorene-co-bis-*N,N*-(4-butylphenyl)-bis-*N,N*-phenyl-1,4-phenylenediamine) (PFB) and poly(9,9-dioctylfluorene-co-*N*-(4-butylphenyl) diphenylamine) (TFB), are blended with three fullerenes: [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), bis-PCBM (where the fullerene cage is functionalized with two methano-bridged PBM side groups), and tris-PCBM (with three PBM side groups). These materials (depicted in Figure 2) result in a range of charge separated state energies from around 1.4 to around 1.8 electronvolts. By using a C₇₀ fullerene, bis-PC₇₀BM, it is possible to study the effect of changes in the absorption spectrum while the LUMO level is unaffected.^[20]

2. Results

The absorption spectra of the three PC₆₀BM fullerenes, dispersed in polystyrene in a 5 wt% concentration are given in Figure 3a. Figure 3b shows the absorption spectra of TFB:fullerene blends, with 50 wt% fullerene in the film, and demonstrates that the blend absorption spectrum appears to arise from a simple superposition of the component spectra without an appreciable contribution from any interfacial ground-state charge transfer complex (although the existence of such a state cannot be ruled out without using more sensitive detection methods^[21,22]).

Figure 4a and 4b show the photoluminescence spectra of pristine TFB and PFB and their blends with the three fullerenes, at 5 wt% loading within the film. All fullerenes strongly quench the polymer emission even at 5 wt% and the quenching values are shown in Table 1. The transient absorption spectroscopy and device measurements were made at higher fullerene loading in the film for optimum results (50 wt% and 80 wt%, respectively), and in these films the quenching of the polymer fluorescence is close to unity (data not shown). No red-shifted exciplex-like emission is observed in the emission spectra of these blend films.^[2,10,11]

Figure 5 presents ultrafast photoluminescence measurements at 460 nm in the polymer:fullerene blends with 80 wt% fullerene (the same blend ratio as used for the devices), showing

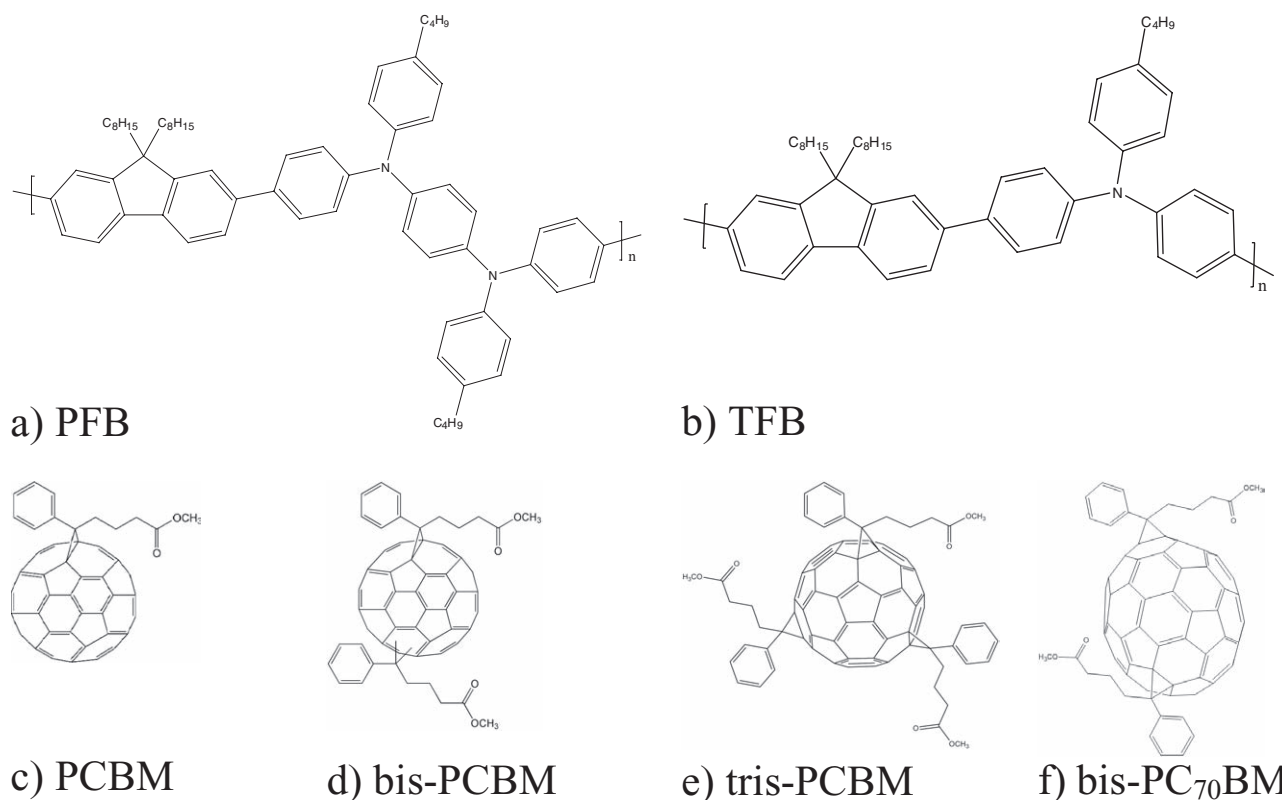


Figure 2. Chemical structures of materials: electron donors PFB (a) and TFB (b), and electron acceptors PCBM (c), bis-PCBM (d), tris-PCBM (e), and bis-PC₇₀BM (f).

the quenching of the polymer photoluminescence. In these films the majority of the quenching occurs prior to the instrument response time of 150 fs, as indicated by the reduced peak emission intensity.

These data indicate that the quenching rate of the polymer photoluminescence is dependent upon the fullerene, with the quenching being highest for PCBM and lowest for tris-PCBM.

However, all the fullerenes studied herein quench the polymer emission strongly, with large amounts of quenching occurring within the temporal resolution of the spectrometer (150 fs).

Excitation spectra for fullerene emission at 720 nm in six polymer:fullerene blends containing 50 wt% fullerene are shown in **Figure 6**. In the PCBM blends there is a small contribution to the fullerene emission from absorption by the

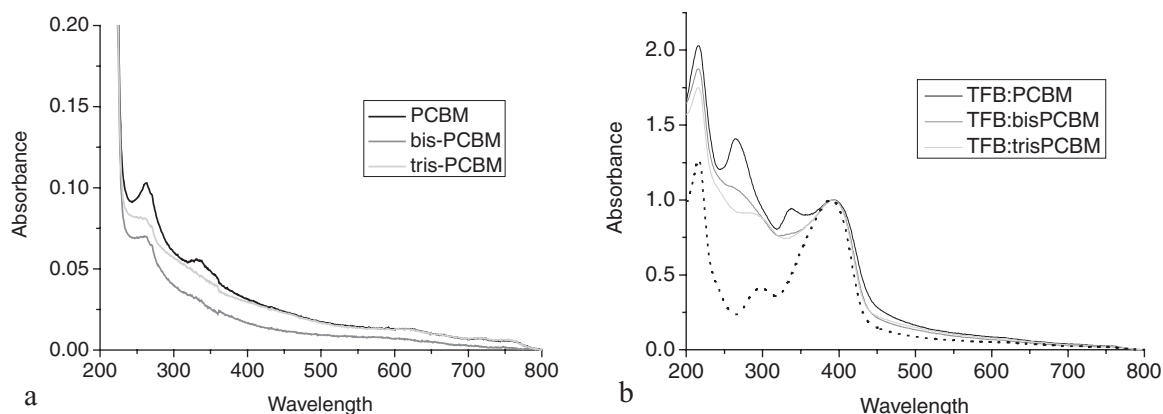


Figure 3. a) UV-vis absorption spectra of 5wt% PCBM (black line), bis-PCBM (dark grey line), and tris-PCBM (pale grey line) in polystyrene. b) Normalized UV-vis absorption spectra of blend films of TFB:PCBM (black line), TFB:bis-PCBM (dark grey line), and TFB:tris-PCBM (pale grey line) (50 wt% fullerene in all cases). Pristine TFB absorption is shown as a dashed line for comparison.

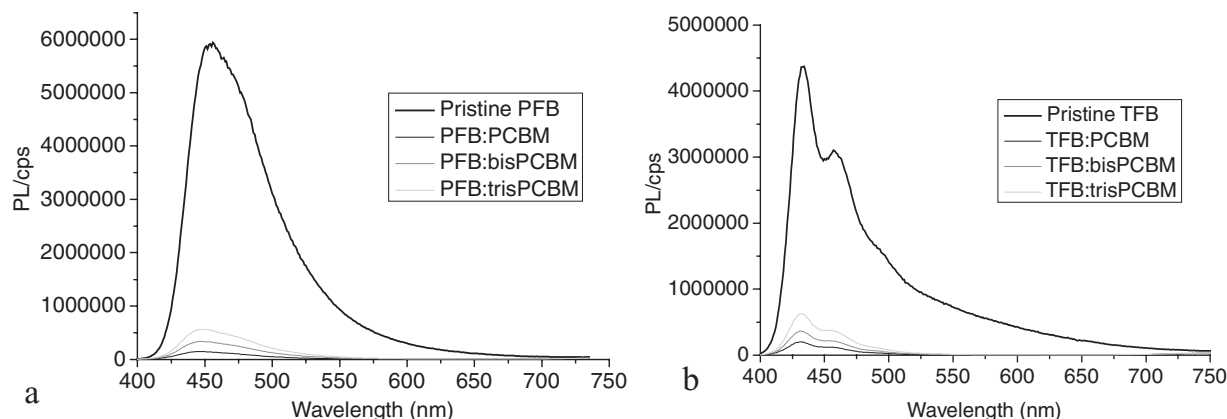


Figure 4. Steady state PL measurement for a) PFB:fullerene blends and b) TFB:fullerene blends at 5 wt% fullerene in all cases. The quenching of the polymer PL is large for all fullerenes albeit decreasing upon the addition of further side groups to the fullerene. At the higher fullerene loadings used in transient spectroscopy (50 wt%) and devices (80 wt%) the quenching is close to unity (not shown)

polymer (between 350 and 400 nm). However, as the number of side groups on the fullerene, and the charge transfer state energy, increases, this peak at 390 nm increases in size, indicating that absorption by the polymer causes emission from the fullerene, i.e. that energy transfer from polymer to fullerene is occurring. Although the total number of emitted photons also increases on going across the fullerene series, the increase in the polymer peak in the excitation spectrum is larger.

To measure the triplet generation yield, transient spectra at 1 μ s following pulsed laser excitation of the polymer:fullerene films containing 50 wt% fullerene were measured at an excitation wavelength of 337 nm. For some blends a large absorption peak at around 720 nm is observed with monoexponential decay kinetics. The same absorption band and kinetics are observed for the pristine fullerene, and so this feature is assigned to the triplet of the fullerene in common with earlier reports.^[3,23,24] In these blends, it is not possible to measure triplets and polymer polarons simultaneously, due to the low

extinction coefficient of the polymer polaron, and the fact that the triplet absorption spectrum of the fullerene overlaps with the broad polaron band from 800–1100 nm.^[12] Therefore in this study we restrict our measurements to detecting the presence of fullerene triplets.

The transient spectra of blend films containing 50 wt% fullerene are shown in Figure 7. The size of the triplet absorption at 720 nm is shown in Table 1 along with the short circuit current for polymer:fullerene devices containing 80 wt% fullerene. Triplet formation is clearly correlated with a decrease in photocurrent (open circuit voltage and fill factors are shown in the Supporting Information). Comparing the triplet absorption with the value of ΔE_{cs} (Table 1) demonstrates that triplet formation occurs at an onset charge separated state energy of around 1.6 eV, in line with previous measurements on polyfluorene:PCBM blends.^[3] These data also show that the specific chemical structure of the fullerene used determines the competition between excited states in the blend, in addition to the energy levels in the system; this can be observed, for example, when comparing the blends of PFB:tris-PCBM and TFB:PCBM, where triplets are observed in the former blend but not in the latter, although they have the same charge separated state energy.

Additional information regarding the origin of the 720 nm absorption feature is available from studying the fullerene dispersed in polystyrene, which is transparent at the wavelengths studied and therefore forms an optically inactive matrix. By comparing the fullerene triplet absorption in this sample and in one with TFB as the matrix (with the fullerene concentration constant at 5 wt%), it is possible to study the relative contribution of the fullerene and the polymer to the triplet population produced in the blend.

When bis-PCBM is dispersed in polystyrene, all triplets are produced by direct fullerene photoexcitation followed by intersystem crossing, giving rise to a monoexponential decay at 720 nm with a lifetime of 40 μ s. When TFB is used to disperse the fullerene, the triplet yield is strongly increased, but the monoexponential lifetime of the transient absorption signal is the same as in the fullerene:polystyrene blend. This additional transient absorption does not arise from the TFB alone, as shown in

Table 1. PL quenching, triplet yield and short circuit currents for polymer:fullerene blends. Pristine polymer emission lifetimes are shown for comparison.

Blend	ΔE_{cs}	PL quenching in 5 wt% fullerene blend	Singlet emission lifetime of polymer [ps]	Triplet ΔOD at 1 μ s (normalized to incident photon absorbance)	Device J_{sc} [mA cm ⁻²]
PFB:PCBM	1.4	97.7	0.57	0.007	0.90
PFB:bis-PCBM	1.5	94.6	1.20	0.02	0.43
PFB:tris-PCBM	1.6	90.9	2.35	0.08	0.03
TFB:PCBM	1.6	95.5	0.72	0.012	0.81
TFB:bis-PCBM	1.7	92.0	1.19	0.206	0.12
TFB:tris-PCBM	1.8	85.9	1.67	0.211	0.00
Pristine PFB	–	–	200	–	–
Pristine TFB	–	–	88	–	–

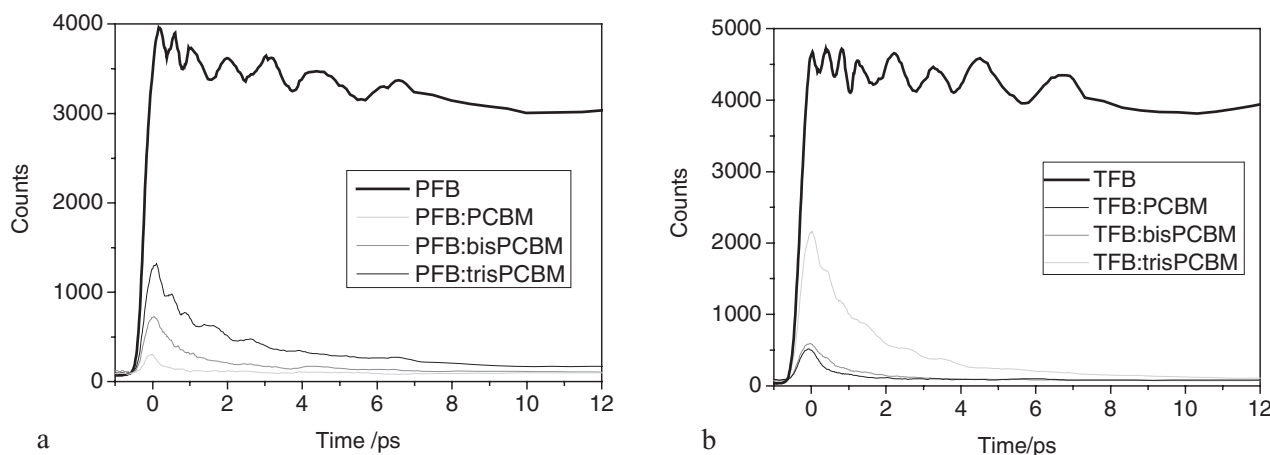


Figure 5. Ultrafast measurement of polymer PL quenching in a) PFB:fullerene and b) TFB:fullerene blends at 80 wt% fullerene, demonstrating fast quenching of the polymer fluorescence by the fullerene acceptor. The reduced peak amplitude demonstrates that a large part of the quenching occurs within the instrument response time of around 150 fs.

Figure 8. This provides strong evidence that direct excitation of the polymer leads to triplet formation in the fullerene.

The increased triplet formation due to polymer excitation is quantified by calculating the percentage increase in the absorption by the triplet state, represented by the change in optical density ΔOD signal for each sample. This permits a comparison between different materials without requiring a calculation of the extinction coefficient for T-T absorption in the fullerenes. When blended with TFB, triplet population in bis-PCBM is increased by a factor of 2.5; in tris-PCBM by a factor of 4.3.

The increase in triplet population on adding TFB, for bis-PC₇₀BM was also measured. C₇₀ derivatives have an increased absorption across the visible spectrum, and for this reason have been used to make efficient solar cells.^[25] The purpose of bisPC₇₀BM in this experiment is in determining the effect of increased fullerene absorption upon triplet formation, to give

insight into the mechanism of triplet formation. In bisPC₇₀BM, the triplet absorption was measured at 1000 nm, and is strongly quenched by oxygen (see Supporting Information for further data on triplet assignment in PC₇₀BM). The decay of the triplet is also slower (lifetime = 300 μ s), but the same trend is observed as for bis-PCBM, and in this case the increase in triplet population produced by TFB excitation is 420%.

3. Discussion

Triplet formation in polyfluorene:fullerene blends appears to result in reduced photocurrent generation, and occurs when the offset between the HOMO of the donor and LUMO of the acceptor is larger than 1.6 eV, as has been shown for a related series of blends by Benson-Smith et al.^[3] The origin of this 1.6 eV energy threshold will depend upon the mechanism of

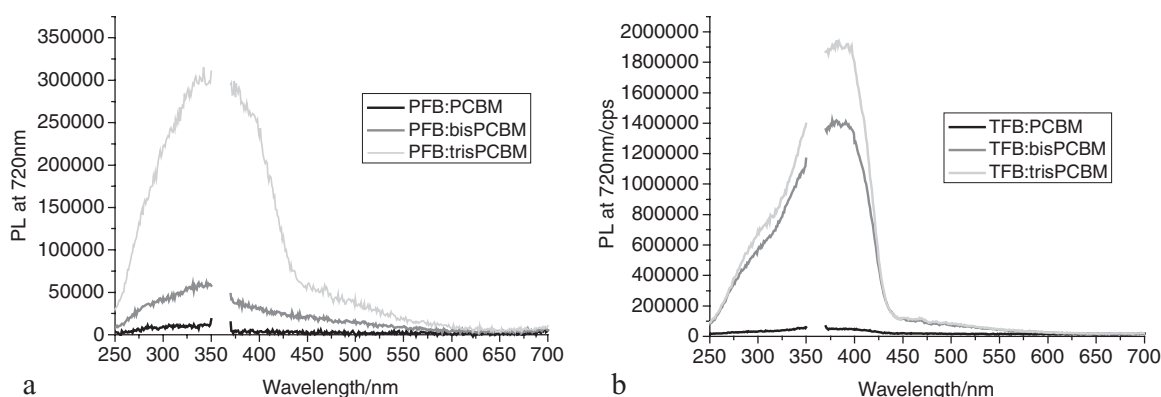


Figure 6. PL excitation spectra for polymer:fullerene blends, measuring emission at 720 nm (corresponding to emission from the fullerene singlet excited state). In all cases the peak in the excitation spectrum corresponds to excitation into the polymer singlet, demonstrating that energy transfer from polymer to fullerene occurs in these blends. The “break” in the data around 360 nm is due to the fact that direct measurement of emission at 720 nm would correspond to the second harmonic of this excitation wavelength and hence would give an erroneous high result at this wavelength.

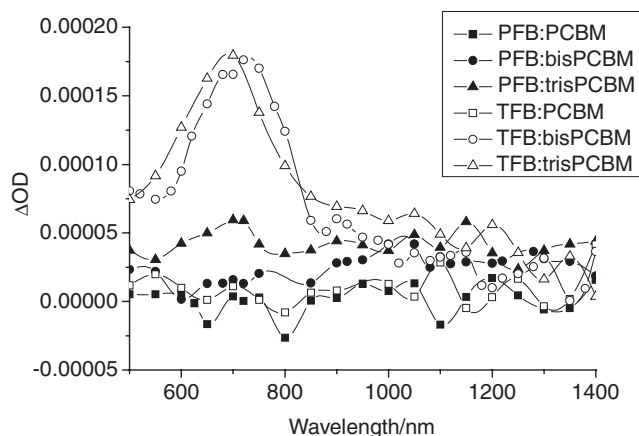


Figure 7. Transient spectra measured at 1 μ s for 50 wt% blends of PFB:PCBM (filled squares), PFB:bis-PCBM (filled circles), PFB:tris-PCBM (filled triangles), TFB:PCBM (open squares), TFB:bis-PCBM (open circles), and TFB:tris-PCBM (open triangles). A peak around 650–700 nm, corresponding to the fullerene triplet, is observed in the PFB:tris-PCBM, TFB:bis-PCBM, and TFB:tris-PCBM blends.

triplet formation at the interface between materials. Different accounts in the literature have assigned triplet formation both to energy transfer and to intersystem crossing within the interfacial charge transfer state.^[3,8,9,14]

We first consider the mechanism of intersystem crossing within the charge separated state (the interfacial bound radical pair), to produce a triplet charge separated state, which can undergo geminate recombination to give a triplet on the polymer or the fullerene. The yield of triplets produced by this process will depend on the dynamics of processes at the interface, in particular the competition between recombination (which would proceed via a hole transfer from the polymer to the fullerene) and full charge pair generation, which will be related to the probability of the charges escaping their mutual Coulombic

attraction. Several recent studies have highlighted domain size and local charge carrier mobility as important determinants of this escape probability and hence charge generation.^[7,12]

The side groups have a strong effect upon the morphology of the fullerenes. Adding side groups to the fullerene cage results in greater disorder and in poorer packing of the fullerene molecules. Figure 3 demonstrates a decrease in vibronic structure in the absorption spectrum, reflecting an increase in packing disorder. In a blend, the bulkier side groups may also influence the specific interactions at the interface between the materials, however the PL measurements presented here indicate that even the most poorly packed fullerene is able to provide a fast deactivation of the polymer fluorescence.

The disordered morphology is also shown by the charge mobility in the materials. Lenet et al. measured the electron mobilities in fullerene blends using the space charge limited current method,^[26,27] and show that the mobility of the fullerene strongly decreases upon adding functional groups, with the electron mobility in tris-PCBM being almost three orders of magnitude lower than in PCBM. The poor performance of devices made with tris-PCBM (with poly(3-hexylthiophene) (P3HT) as the donor) to be ascribed to the low mobility and electron trapping in the blend.

Structural and energetic disorder will also arise as a result of the large number of different regioisomers of the bis and tris fullerenes. The different isomers will result in different energy levels, and although the energy level values quoted here are measured experimentally, they represent a weighted average of all the different possible isomers. This means that for the bis and tris fullerenes, there exist higher and lower energy states (singlets, triplets or charge-transfer states) that may lead to a variety of different reactions upon photoexcitation. This has recently been confirmed by electrochemical measurements in which the first reduction peak broadens across the series of fullerenes as the number of side groups increases.^[28]

An alternative mechanism for triplet formation in the fullerene involves energy transfer from the photogenerated

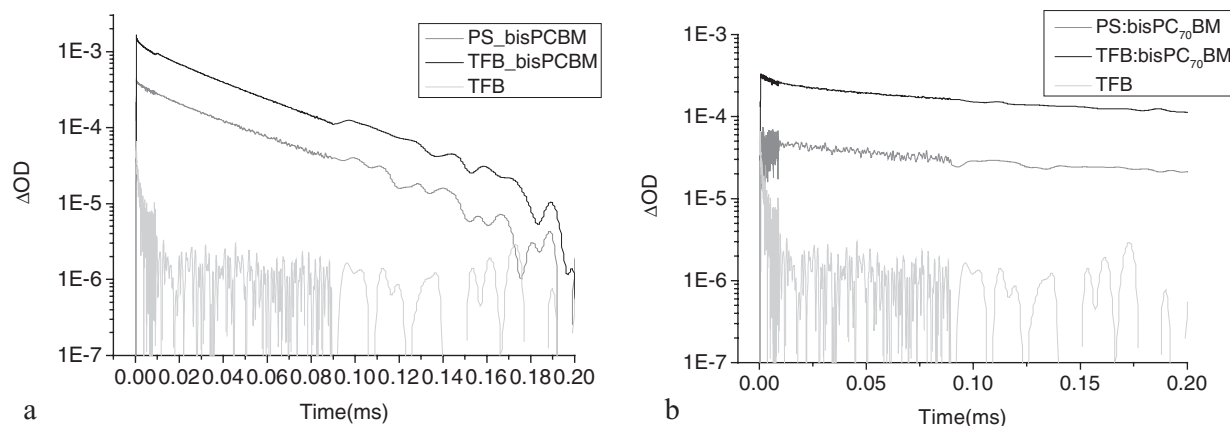


Figure 8. a) Transient decay kinetics of fullerene triplet absorption at 720 nm for films of 5 wt% bis-PCBM dispersed in polystyrene (dark grey line) and TFB (black line). b) Transient decay kinetics of fullerene triplet absorption at 1000 nm for films of 5 wt% bis-PC₇₀BM dispersed in polystyrene (dark grey line) and TFB (black line). The triplet absorption increases in intensity upon excitation of the donor polymer (this is not accounted for by the transient absorption of the polymer alone, pale grey line). All measurements were performed with an excitation wavelength of 337 nm.

polymer singlet to the fullerene singlet, followed by intersystem crossing to the fullerene triplet. From the transient spectroscopic measurement of fullerene dispersed in a TFB or a polystyrene matrix, we concluded above that excitations are transferred from the polymer to the fullerene. There could also be some transfer of excitation from the photoexcited fullerene to the polymer, via a hole transfer reaction; the existence of such a mechanism is supported the fact that photocurrent generation occurs by light absorption in the fullerene, as was observed in a recent study of P3HT:PCBM bilayer devices^[29] and in a P3HT:PCBM blend.^[30] However, deactivation of the fullerene by hole transfer to the polymer, would lead to a net decrease in the intersystem crossing yield, and so would lead to an underestimate of the increase due to light absorption in the polymer.

Photocurrent generation by direct fullerene excitation also implies that selective excitation of the fullerene would lead to a geminate pair at the interface that could undergo dissociation or recombination to a singlet or a triplet. Repeating the measurement in Figure 8, but using an excitation wavelength of 500 nm (where absorption by the polymer is expected to be weak), shows no increase in triplet yield upon adding the donor polymer, indicating that recombination from a triplet interfacial charge transfer state to a fullerene triplet (process g in Figure 1) is not an important pathway in this system. This data is shown in the Supporting Information.

A more compelling argument for the energy transfer mechanism is available by considering the Förster theory for resonant energy transfer, which expresses the transfer rate k_{ET} in terms of the intermolecular separation of energy donor and acceptor and the spectral overlap between the emission of the donor and the absorption of the acceptor. In the simplest form, the Förster equation states that the rate of energy transfer is directly proportional to the spectral overlap. In a donor-acceptor blend film the assumptions in simple Förster theory are not valid, and the dependence of the rate upon the spectral overlap may not be linear^[31]; nonetheless, an increased spectral overlap will lead to increased energy transfer.

The increase in triplet yield caused by the addition of donor was compared for blends of TFB with a C_{60} derivative, and with a C_{70} derivative. In both cases, the bis-PCBM fullerene was used, since this is a blend with $\Delta E_{CS} > 1.6$ eV, and hence will exhibit triplet formation if the energy transfer mechanism is correct. Figure 9 clearly shows that when the spectral overlap between polymer emission and fullerene absorption is increased (by the use of C_{70}), polymer excitation produces relatively more triplets on the fullerene, than when a blend with a lower spectral overlap is used. This implies that energy transfer from polymer to fullerene is a step in the formation of triplets.

We also note that the electron mobility of the C_{70} derivative may be lower than in PC₆₀BM,^[32] and that this may increase triplet formation by the geminate recombination mechanism. However, a recent study in field-effect transistors has demonstrated comparable mobilities for the two materials.^[33] In addition, when the triplet increase is compared between bis- and tris-PCBM, where the charge mobilities differ by two orders of magnitude, the increase in triplet yield is comparable to that between C_{60} and C_{70} , indicating that the change in mobility does not have a large effect in the latter comparison.

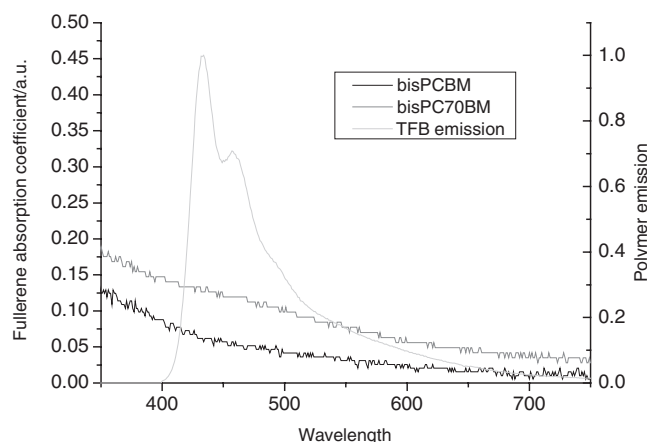


Figure 9. Absorption coefficient spectra of bis-PCBM (black line) and bis-PC₇₀BM (dark grey line), both measured at 5 wt% in a polystyrene matrix, and normalized emission spectrum of TFB (pale grey line). The increased absorption of bis-PC₇₀BM in the visible spectrum results in a greater spectral overlap integral.

The PL excitation spectra show that on going across the C_{60} fullerene series, the amount of fullerene emission increases on increasing the number of side groups on the fullerene and is largest for those blends with high triplet yield –this strongly indicates that energy transfer and triplet formation occur together. The amount of energy transfer, as indicated by the size of the “polymer” peak in these excitation spectra, is larger for TFB than for PFB, supporting the conclusion that energy transfer is favoured when the charge separated state energy is high.

4. Conclusions

Triplet formation is observed in polymer:fullerene blends with high charge-transfer state energies and is associated with a loss of photovoltaic performance, ascribed to the competition between charge-pair and triplet formation. In a series of polyfluorene:fullerene blends, triplet formation occurs when the offset between the donor IP and acceptor EA is larger than 1.6 eV, supporting the work of earlier studies on related polymer:fullerene blends.^[3] Triplet formation appears to occur via two mechanisms; geminate recombination of triplet charge-transfer states, which is increased for low-mobility bulky fullerenes, and direct polymer-fullerene energy transfer followed by intersystem crossing. This indicates that the charge-transfer state energy, geminate recombination and the spectral overlap between blend components are all important parameters in triplet formation, and should be taken into account when designing new material combinations for organic photovoltaics.

5. Experimental Section

PCBM, bis-PCBM, tris-PCBM and bis-PC₇₀BM were obtained from Solenne BV. PFB and TFB were obtained from Sumitomo Chemical Company, and polystyrene (PS) obtained from Aldrich. All materials were dissolved in chlorobenzene to a concentration of 10 mg/ml. Blend solutions were made by combining the individual solutions at PCBM

concentrations of 5, 50, and 80 wt%, resulting in a total blend solution concentration of 10 mg mL⁻¹ in all cases. Films for spectroscopy were deposited by spincoating at 1500 rpm for 30 s onto Spectrosil B fused quartz substrates (12 × 12 mm, UQG Optics), cleaned by sonication in acetone followed by IPA for 10 min each. Devices were made by spincoating 80 wt% fullerene solutions onto acetone and IPA cleaned indium tin oxide (ITO) substrates, which had previously had a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, H.C. Starck Baytron P, 60 nm) applied. Aluminium electrodes 60 nm in thickness were then applied by thermal evaporation.

Absorption spectra were measured using a Shimadzu UV-2550 spectrophotometer, and steady state photoluminescence spectra (in emission and excitation modes) were measured with a HORIBA Jobin Yvon Fluorolog-3 spectrofluorimeter. Photoluminescence excitation spectra were measured for emission at 720 nm corresponding to the fullerene emission, using the same spectrofluorimeter. The photoluminescence dynamics in polymer:fullerene films were studied using a femtosecond fluorescence upconversion technique. The samples were excited by a frequency-doubled output from an ultrafast mode-locked Ti:Sapphire oscillator (Newport Spectra-Physics Broadband MaiTai). Excitation and gate wavelengths were fixed at 400 and 800 nm, respectively. Both the gate and excitation beams were independently compressed using prism pair compressors. The excitation intensity was adjusted to be below the onset of intensity dependent kinetics. Photoluminescence from the sample was focused on a 200 μm thick BBO crystal along with the 800 nm gate beam. Sum frequency generated photons (corresponding to photoluminescence at 460 nm) were detected using a photomultiplier tube (R7207-01, Hamamatsu) and data was acquired using LabView software (Ultrafast Systems). The temporal resolution of the system was 150 fs. Sample degradation was avoided by performing the measurements under flowing nitrogen and using a translation stage to move the sample within the beam, removing the effect of photobleaching and providing data averaged across the whole of the sample.

For all TAS measurements, three identical samples were stacked together in the path of the pump and probe lights in order to increase the signal size. TAS was performed with an excitation wavelength of 337 nm using a GL-3300 nitrogen laser (Photon Technologies International, intensity ~200 μJ cm⁻²), and all experiments were performed in sealed nitrogen-filled cuvettes unless otherwise stated.

Current–voltage characteristics for devices were measured using a Keithley 237 high voltage source measure unit over a device area of 0.045 cm², and were averaged over between four and six devices.

Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

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