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Understanding Triplet Formation Pathways in Bulk Heterojunction Polymer:Fullerene Photovoltaic Devices

Biniam Zerai Tedlla, Feng Zhu, Matthijs Cox, Jeroen Drijkoningen, Jean Manca, Bert Koopmans,* and Etienne Goovaerts*

Triplet exciton (TE) formation pathways are systematically investigated in prototype bulk heterojunction (BHJ) “super yellow” poly(p-phenylene vinylene) (SY-PPV) solar cell devices with varying fullerene compositions using complementary optoelectrical and electrically detected magnetic resonance (EDMR) spectroscopies. It is shown that EDMR spectroscopy allows the unambiguous demonstration of fullerene triplet production in BHJ polymer:fullerene solar cells. EDMR triplet detection under selective photoexcitation of each blend component and of the interfacial charge transfer (CT) state reveals that low lying fullerene TEs are produced by direct intersystem crossing from singlet excitons (SEs). The direct CT-TE recombination pathway, although energetically feasible, is kinetically suppressed in these devices. However, high energy CT states in the CT manifold can contribute to the population of the fullerene triplet state via a direct CT-SE conversion. This undesirable energetic alignment could be one of the causes for the severe reduction in photocurrent observed when the open-circuit voltage of polymer:fullerene solar cells is pushed to 1.0 V or beyond.

efficiency of charge separation. Despite the encouraging progress in power conversion efficiency the photophysics is not yet fully understood. In particular, the role of the charge transfer (CT) and triplet states occurring at the interface between the polymer and fullerene of BHJ device in the underlying photovoltaic mechanism and their effect on the photovoltaic properties is not fully clarified.

Photoexcitation of the optically active layer of polymer:fullerene BHJ device produces thermalized and bound singlet excitons (SEs) both in the polymer and fullerene domains due to the low dielectric permittivity compared to inorganic semiconductors. SEs within their typical diffusion length of $\approx 5\text{--}10$ nm can reach the interface and convert to charge transfer (CT) pairs by forward electron and/or reverse hole transfers from the polymer and/or the fullerene domains, respectively.^[4–7]

A stabilized CT pair consists of a Coulombically interacting hole in the polymer domain with an electron in the proximate fullerene domain. The interfacial CT states are a result of a spatial overlap in wave functions of donor and acceptor materials. Direct optical excitation from the ground state to CT states have been first confirmed in BHJ solar cell based on poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene](MDMO-PPV):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and regioregular poly(3-hexylthiophene)(P3HT):PCBM.^[8–10]

An interfacial CT pair in a donor:acceptor blend may i) dissociate to separated charge carriers, ii) recombine to the ground state, iii) decay to a low lying triplet state of one of the composite materials, or iv) become trapped and involved in trap-assisted recombination process.^[5,8,11–17] Some of the relevant interactions have been studied in relation with the organic magnetoresistance (OMAR) effect in polymer:fullerene BHJ devices of varying composition.^[18,19] The photophysical pathways in which the CT pair can evolve are determined by two interrelated factors: the energy of the CT state, E_{CT} , relative to that of other excited states and the competing probabilities for possible interfacial relaxation and decay processes. Both these energetic and kinetic factors are dependent on the physical properties of the component materials and the degree of their interfacial intermixing.

In a number of efficient BHJ polymer:fullerene solar cells where E_{CT} is higher than the energy of the triplet state of one

1. Introduction

The recent surge in power conversion efficiency of polymer:fullerene based bulk heterojunction (BHJ) solar cells, close to the 10% threshold value considered for commercialization, make them promising alternatives to conventional inorganic solar cells.^[1–3] The enhancement in efficiency is mainly due to engineering of novel donor polymers with improved energetic alignment between their photon absorption range and the solar spectrum, and optimizing interfacial quantum

B. Z. Tedlla, Prof. E. Goovaerts
Physics Department
University of Antwerp
Universiteitsplein 1, B-2610, Antwerpen, Belgium
E-mail: Etienne.Goovaerts@uantwerp.be

Dr. F. Zhu, M. Cox, Prof. B. Koopmans
Department of Applied Physics
Center for Nanomaterials (CNM)
Eindhoven University of Technology
5600, MB, Eindhoven, The Netherlands
E-mail: B.Koopmans@tue.nl
J. Drijkoningen, Prof. J. Manca
ONE² group
Hasselt University
Wetenschapspark 1, 3590, Diepenbeek, Hasselt, Belgium

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or both of the component materials, the formation of triplet excitons (TEs) is assigned to i) decay of CT pairs in triplet (^3CT) state to an energetically low lying triplet state, ii) direct decay of SEs to TEs by intersystem crossing (ISC), or iii) TE-TE energy transfer between donor and acceptor, or to a combination of these processes. Recent studies^[20,21] considered path (i), involving specifically low-lying triplet states in the polymer, in BHJ poly[indacenodithiophene-co-phenanthro[9,10-b]quinoxaline](PIDT-PhanQ):fullerene solar cells as a possible terminal charge loss pathway, looking for the origin of the much lower efficiency obtained when PCBM was replaced by indene-C60 bisadduct (ICBA) as fullerene acceptor. In an earlier study Schlenker et al.^[21] concluded that losses through direct transition from CT exciton to polymer TE were not important and that a new loss channel was opened upon replacement of acceptor by alignment of CT level with the TE energy in ICBA and consecutive TE-TE transfer towards the polymer, illustrating path (ii). In a broader study, Rao et al.^[20] showed that this should be attributed to competition between path i) from CT towards the low-lying polymer TE and, faster or slower (for PCBM and ICBA, respectively) processes for charge separation of the triplet CT exciton. Di Nuzzo et al. assigned all three pathways to describe triplet formation in BHJ films composed of poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PF10TBT) blended with different types of fullerenes.^[22] In a number of inefficient BHJ wide bandgap polymer:fullerene blend devices where the CT state is not involved in charge separation, fullerene TE formation is attributed to a two steps process: SE formation in fullerene domains by energy transfer (ET) and TE formation from the SEs by ISC. Since this process by-passes the intermediate CT state, it is considered a terminal charge-loss pathway.^[23,24]

It therefore appears there is no clear consensus on TE formation pathways in BHJ polymer:fullerene system, and their impact on interfacial charge separation. Towards a better understanding of the role of TEs in polymer:fullerene systems, we systematically explore the interfacial photophysics in a wide bandgap donor (co)polymer “super yellow” poly(p-phenylene vinylene) (SY-PPV) blended with one of three fullerene acceptors: PC(70)BM^[25] or ICBA, and present competing CT and TE formation pathways. We modulate the E_{CT} by varying SY-PPV:fullerene composition as well as the energy of the lowest unoccupied molecular orbital (LUMO) of fullerenes. SY-PPV is selected as a donor polymer in this study due to its high reproducibility during device fabrication, and its high photoluminescence (PL) quantum yield allows the investigation of competitive ET processes.^[26] The SY-PPV:fullerene blend combination permits selective photoexcitation of the polymer, fullerene and CT states. Combining selective photoexcitation with electrically detected magnetic resonance (EDMR) experiments, we unambiguously identify the photophysical pathways that lead to the formation of fullerene TEs.

2. Results and Discussion

In Figure 1a,b the chemical structures of SY-PPV, PCBM, PC70BM and ICBA, and their highest occupied molecular orbital (HOMO)–LUMO energy level band diagrams are shown. The HOMO and LUMO energy levels of ICBA are ≈ 0.18 eV higher than the corresponding levels of PCBM or PC70BM, keeping the same electronic bandgap between the fullerene materials.^[27] SY-PPV forms a type-II band alignment with PC(70)BM, which generally favors charge transfer at the polymer:fullerene interface.

Figure 1. a) The chemical structure of SY-PPV, PCBM, PC70BM and ICBA. b) The corresponding HOMO–LUMO energy band diagram.^[5,68] c) The normalized absorption spectra of spin-coated films of pristine SY-PPV and of (20:80) blends of SY-PPV:PCBM, SY-PPV:PC70BM, and SY-PPV:ICBA.

Figure 2. PL spectra (semilogarithmic scale) of films of blends with varying compositions of a) SY-PPV:PCBM, b) SY-PPV:PC70BM, and c) SY-PPV:ICBA, and of the pristine components, photoexcited at 2.77 eV ($\lambda_{\text{laser}} = 447$ nm) in the SY-PPV absorption band. Vertical arrows mark the approximate peak position of the PL contributions from the SY-PPV and fullerene components and from the CT emission (only in PC(70)BM) at ≈ 2.3 eV, ≈ 1.7 eV and ≈ 1.5 eV, respectively. Only the spectra from the pristine fullerenes have been rescaled relative to the other spectra in order to facilitate comparison with the other curves.

Figure 1c depicts the normalized absorption spectra of films of pristine SY-PPV, and of blends of SY-PPV and the three fullerenes (at maximum fullerene loading). The pristine SY-PPV film has a broad absorption band with a maximum at 2.76 eV. Except for in SY-PPV:PC70BM of high PC70BM loading, the absorption spectra of the blend films are dominated by the SY-PPV absorption band due to the relatively weak absorption capability of fullerenes. In the following sections, we apply PL, electroluminescence (EL) and time-resolved PL to investigate interfacial photophysical processes in blend films. Finally, we apply the EDMR technique to detect TE formation under different photoexcitation energies.

2.1. Emission from Excitonic and Charge Transfer States: Photoluminescence

Figure 2 shows the PL spectra of both the SY-PPV:fullerene blend and the pristine films of each component. Except for the rescaled spectra (bottom curves) of the pristine fullerene films, the relative intensities between films are meaningful. In the blend films, the fullerene concentration, expressed by weight ratio percentage (w/w), varies from 1% to 80%. All films are photoexcited at 2.77 eV ($\lambda_{\text{laser}} = 447$ nm), close to the absorption peak of the pristine SY-PPV film. The PL spectrum of pristine SY-PPV has a peak at 2.30 eV, and a weak vibronic shoulder at 2.10 eV. The peaks of the PL spectra from the three pristine fullerene films vary between 1.68–1.72 eV. The profile of the PL spectra of the blend films differs for low (w/w < 10%), and high (w/w $\geq$ 10%) fullerene concentrations due to variation in relative

fluorescence contribution from each material component of the blend, and of their heterojunction interface.

In SY-PPV:fullerene blend films of low fullerene concentrations, the fullerenes are distributed uniformly in the polymer films with minimal aggregate formation. When these films are photoexcited, the resulting PL is entirely from the SY-PPV polymer. However, the intensity of the SY-PPV PL very drastically reduces with increase in fullerene concentration (e.g., at 3% w/w, PL intensity is reduced to $\approx 10\%$). No additional PL bands emerge in the PL spectra, or if present, they are overwhelmed by the polymer fluorescence. At such low fullerene concentrations, the quenching of the polymer PL is mainly due to ET to the weakly emissive fullerene molecules.^[23,24,28] The ET is favored by the homogenous intermixing of the fullerenes in SY-PPV layer, and the strong spectral overlap between the fluorescence band of SY-PPV and the absorption range of fullerenes.^[29]

In SY-PPV:PC(70)BM blend films of high fullerene concentration, a further reduction in the polymer PL (3–4 orders of magnitude for 50–80% fullerenes) is accompanied by the emergence of a broad low energy PL band. This new PL band is different from the PL bands of the pristine films of the component materials, and is assigned to radiative recombination of interfacial charge pairs in the CT states as already reported in other polymer:fullerene blends.^[6] The redshift in the peak position of the CT PL band with PC(70)BM concentration in the blend is attributed to increment in dielectric permittivity of the interfacial environment, and/or improvement in local interfacial fullerene ordering that promotes charge delocalization.^[23,28,30,31] In SY-PPV:PC(70)BM blend films with $\geq 50\%$ fullerene concentration, where the polymer emission is nearly fully quenched,

the CT PL band peaks at 1.52 eV. On its high-energy flank an overlapping band forms a shoulder at 1.69 eV and 1.72 eV in SY-PPV(50:50)PC70BM, and SY-PPV(20:80)PCBM, respectively. This band is at nearly the same energetic position as the PL peak in the pristine PC(70)BM film, and is therefore assigned to radiative recombination of SEs in PC(70)BM domains mostly originating from regions close to the interface. The spectral overlap between the CT and PC(70)BM fluorescence bands imply energetic matching between high energy CT states in the CT manifold and the PC(70)BM singlet states.

In SY-PPV:ICBA blend films of high ICBA concentration, the PL band of the ICBA is clearly visible and its peak energetic position approaches the PL peak position of pristine ICBA film with increasing ICBA concentration. No interfacial CT PL band is observed for this blend combination. Raising the fullerene LUMO (see Figure 1b) and as a result the E_{CT} by 0.18 eV to ≈ 1.70 eV by using ICBA as an acceptor component in the blend, the CT states render themselves inaccessible for steady population, inhibiting interfacial radiative CT recombination and dissociation processes. Interestingly, the polymer PL quenching efficiency of ICBA in SY-PPV:ICBA is comparable to that of PC(70)BM in SY-PPV:PC(70)BM blends (see Supporting Information Figure S1). Such an efficient PL quenching by ICBA without effective charge separation, suggests very efficient ET from SY-PPV to ICBA domain across the interface and intimate intermixing between SY-PPV and ICBA components. However, the polymer PL quenching efficiency of ICBA tends to saturate at high ICBA w/w concentration due to a possible saturation of molecular mixing.

It appears that the peak of the PL band of SY-PPV blueshifts in energy with fullerene concentration in blend films. In different fluorene based polymer:fullerene blend films which exhibit efficient ET^[23,24,28] such a shift has been attributed to sensitive morphological variations of polymer domains when blended at increasing fullerene concentration. In this investigation, a blueshift in the peak of the SY-PPV band is observed upon blending of SY-PPV with any of the three fullerenes. Therefore, the blueshift is most likely due to a combination of material dependent sensitive morphological adjustment of the polymer to the presence of fullerenes, and selective emission from higher vibrational states when relaxation is in competition with quenching processes such as charge or energy transfer.

Photoexcitation of BHJ blend films of SY-PPV(50:50)PC(70)BM at 1.89 eV ($\lambda_{laser} = 655$ nm), well outside the absorption range of SY-PPV, reveals CT PL bands with shoulder similar to that for above-bandgap photoexcitation (see Supporting Information Figure S2). The CT states are populated via the relaxation of fullerene SEs at the interface by reverse hole transfer from the PC(70)BM to SY-PPV domains driven by the HOMO-HOMO energy difference. There could also be a contribution to the CT PL band from direct photoexcitation of the CT state at this photoexcitation energy. The high energy PL shoulders, as is observed for above bandgap excitation at these compositions, are due to radiative recombination of SEs in PC(70)BM domains. Similar optical excitation of SY-PPV(50:50)ICBA blend film shows the ICBA PL band that is attributed to radiative recombination of SEs in the ICBA domains. Formation of CT pair by reverse hole transfer is prevented because of the higher energy of the CT states compared to the singlet energy

of ICBA. Therefore, SEs are formed as a result of direct photoexcitation in the ICBA domains, and swift transfer of any CT pair formed by direct photoexcitation to singlet states in ICBA domain. The latter is corroborated by the EL data discussed below. To summarize, the low energy PL band of the CT states in SY-PPV:PC(70)BM blends are detected when either of the material component is photoexcited. CT pairs are formed by either forward electron or reverse hole transfer across the heterojunction interface. The high energy PC(70)BM shoulders in the PL spectra are due to SE recombination in fullerene. CT emission is not observed in SY-PPV:ICBA blend films which is attributed to the relatively high energy of the CT states that prevents steady state population.

2.2. Recombination of Injected Charge Carriers: Electroluminescence

EL results from radiative recombination of electrons and holes injected into the photo-active layer from the electrodes of a BHJ device. In devices of low fullerene concentration, the majority of electrons and holes are injected into the pervasive SY-PPV component. Opposite charges, within the Coulomb radius, form electron-hole pairs that may bind into excitonic states. Eventually, the SEs recombine radiatively to yield the EL band of SY-PPV, or in the presence of proximate fullerene molecules convert into fullerene SEs by ET. The fullerene SEs can also recombine radiatively giving rise to the fullerene EL band (see Figure 3). A small percentage of the injected electrons and holes (near the negative electrode) may also meet at molecular contact sites of SY-PPV and fullerene to form CT charge pairs. These charge pairs radiatively recombine to give the distinctive low energy EL band of the CT states, as is observed in SY-PPV:PC(70)BM devices. However, in SY-PPV:ICBA devices of low ICBA concentration, before interfacial CT recombination charge pairs in the CT state efficiently convert into SEs in ICBA near the interface, as the CT energy is equal to or higher than that of the SE in ICBA.

In devices of high fullerene concentration under low forward bias voltages, electrons and holes are injected preferentially into the fullerene and SY-PPV domains, respectively.^[61] In the presence of quasi-bicontinuous pathways for both types of charges, the injected charges are likely to meet and form CT pairs at the interface. In SY-PPV:PC(70)BM devices of high PC(70)BM concentration, the EL emission from the SY-PPV domains is completely quenched, while the EL CT band is distinctively visible. Very weak EL shoulders at high energy (approximately at similar spectral position to the PL measurement) are due to radiative recombination of SEs in the PC(70)BM domains. Here the SEs are formed entirely from the CT charge pair precursors. The PC(70)BM EL emission is weak as a result of a combination of i) relatively low population of higher energy CT states by charge injection, with ii) a punitive interfacial HOMO-HOMO energy barrier holes must tunnel through. The same phenomena as discussed for the PL spectra would also lead to the redshift of the EL CT band. In SY-PPV:ICBA devices of high ICBA concentration, the energy of the low lying states in the CT manifold is still at or above the singlet energy of ICBA, and all CT pairs swiftly move to the ICBA domain where they may radiatively recombine to give the EL band of ICBA. Direct injection

Figure 3. EL spectra of BHJ a) SY-PPV:PCBM, b) SY-PPV:PC70BM, and c) SY-PPV:ICBA blend devices are shown together with that of a SY-PPV diode device. The spectra are arbitrarily rescaled for easiest comparison of the spectral components originating from SY-PPV, fullerene and from the CT transition which are marked by vertical arrows (at ≈ 2.3 eV, ≈ 1.7 eV and ≈ 1.5 eV, respectively). Vertical arrows mark the position of the contributions from the SY-PPV and fullerene components and from the CT emission (only in PC(70)BM) at ≈ 2.3 eV, ≈ 1.7 eV and ≈ 1.5 eV, respectively. We note that the EL CT peak of SY-PPV(20:80)PCBM appears to be slightly shifted to higher energy. This is probably related to variation in spin coating conditions between devices.^[69] Charges are injected into the active layer of the devices at 3.0 V except when marked by *, **, and ***, where 1.3 V, 1.5 V, and 1.8 V are applied, respectively.

of holes to ICBA domains due to a higher HOMO level and recombination with electrons thereafter may also contribute to the EL band of ICBA.

2.3. Lifetime of Excitonic and CT States: Time-Resolved Photoluminescence

Time-resolved PL measurements have been performed to compare the lifetimes of SEs and CT pairs in blend films of SY-PPV:fullerene, and of the SEs in pristine materials at different emitted photon energies. All films are photoexcited with picosecond laser pulses at 3.10 eV ($\lambda_{\text{laser}} = 400$ nm). **Figure 4** shows the PL decay of radiative species in films of SY-PPV, the fullerenes, and their blends of varying compositions. The PL trace of pristine SY-PPV detected at 2.30 eV shows a multiexponential decay with an effective lifetime constant (the $1/e$ value τ_{eff}) of 1.2 ns. The PL decay of pristine fullerene films is within experimental uncertainty monoexponential with lifetimes of 1.18 ns, 0.79 ns, and 1.08 ns for PCBM, PC70BM, and ICBA, respectively. Identical lifetimes are determined in each fullerene film at 1.72 eV and 1.52 eV (see Supporting Information Figure S3).

Increasing the concentration of PC(70)BM in SY-PPV:PC(70)BM blend films increasingly quenches SEs of SY-PPV, prior to full internal thermalization, due to their relaxation towards the CT state, or conversion to SEs in the PC(70)BM domains by ET. Increasing the ICBA concentration in SY-PPV:ICBA blend films also drastically decreases the lifetime of SEs in

SY-PPV due to ET (see **Figure 4a** and Supporting Information Figure S4). In SY-PPV(20:80)PC(70)BM blend films, the weak residual SY-PPV fluorescence has a decay time close to the instrumental response (≈ 40 ps) at probe energy of 2.30 eV. Since the residual PL from SY-PPV domains is negligible at photon energies ≈ 1.52 eV, it is now possible to selectively probe the lifetime, τ , of CT pairs. The CT state fluorescence displays a mono-exponential decay with τ longer than that of the pristine PC(70)BM films (see **Table 1**) as is clearly seen for the blends with PC70BM in **Figure 4c**. The CT lifetimes are in the range of previous reports of $\tau \approx 0.5$ ns in poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)](PCPDTBT):PCBM,^[32] and of $\tau \approx 3$ ns in PF10TBT:fullerene.^[22] Selective measurement in the corresponding blend films of the fullerene SE fluorescence at energy 1.72 eV is hampered by the overlap with the CT emission and by the residual fluorescence from the SY-PPV domains.

However, an insight into the τ 's of radiative species in PC(70)BM domain in the blend films could be gained from that of radiative ICBA species in SY-PPV:ICBA blend films. At $E = 1.72$ eV, τ of the ICBA PL in the blend films approaches that of the pristine ICBA film ($\tau = 1.06$ ns) with increasing ICBA concentration in the blend. Similarly, the τ 's of the radiative SEs in fullerene domains in SY-PPV:PC(70)BM blend films are expected to approach those of the pristine PC(70)BM films with increasing concentration (with the emergence of domains). Charge and energy transfer processes, that lead to population

Figure 4. Time resolved PL of pristine SY-PPV and SY-PPV:fullerene blend films detected at two different probe energies of 2.30 eV and 1.52 eV, under pulsed laser excitation at 3.10 eV ($\lambda_{\text{laser}} = 400$ nm). a) Decay of polymer SEs emission in SY-PPV:PCBM blend films of different concentrations detected at 2.30 eV. Decay of CT state emission at $E = 1.52$ eV in b) SY-PPV:PCBM and c) SY-PPV:PC70BM blend films. For comparison the decay traces of pristine PCBM and PC70BM films detected at 1.72 eV (grey lines) are included. Similar comparison of d) SY-PPV:ICBA emission at 1.52 eV with pristine ICBA PL decay trace detected at 1.72 eV (grey line).

of the singlet states in the fullerene domains and of the interfacial CT states, are ultrafast ($\approx 30\text{--}50$ fs)^[12,33] and have little contribution to τ of radiative species. The CT state in the blends with PC(70)BM is an intermediate level in the photophysical processes with lifetime longer than that of SEs in the fullerene domain (and evidently much longer than for the quenched SEs in the polymer).

2.4. Identification of Triplet States: Electrically Detected Magnetic Resonance

Excitons that do not dissociate or recombine to the ground state feed into other competitive charge loss pathways, including low lying triplet states of one of the constituting materials. TEs in polymer:fullerene devices can be unambiguously identified by the highly sensitive EDMR technique. The identification is based on their spectral profiles which are related to the zero-field splitting interaction,^[34–36] unlike the traditional photoinduced absorption and phosphorescence techniques that generally suffer from spectral overlap with other species and from trap-mediated delayed fluorescence, respectively.

Table 1. Experimental decay times (in ns) of the CT emission in the (50:50) and (20:80) films of SY-PPV:PC(70)BM compared to those of the fullerene SE emission in the corresponding SY-PPV:ICBA blends and in pure fullerene.

Blend ratio	PCBM	PC70BM	ICBA	
50:50	2.14 ^{a)}	1.20 ^{a)}	1.39 ^{a)}	1.31 ^{b)}
20:80	1.62 ^{a)}	1.01 ^{a)}	1.16 ^{a)}	1.12 ^{b)}
0:100	1.18 ^{b)}	0.79 ^{b)}		1.08 ^{b)}

^{a)}Detected at 1.52 eV; estimated error ± 0.08 ; ^{b)}Detected at 1.72 eV; estimated error ± 0.02 .

In EDMR one detects change in current through an electrical device when spin magnetic resonance conditions are satisfied. EDMR has previously been applied to study recombination of polarons in MDMO-PPV:PCBM,^[34] TEs in organic light-emitting devices,^[37–39] and interfacial defects in a number of inorganic solar cell devices.^[40–42] In this investigation, we detect the resonance change in photocurrent (also called photo-EDMR) in the SY-PPV:fullerene devices under short circuit conditions.

Figure 5 shows the photo-EDMR spectra of SY-PPV:fullerene blend and pristine polymer devices under photoexcitation at 2.77 eV. The spectrum in a pristine SY-PPV diode consists of an intense and sharp central peak at a field position corresponding to a value of the gyroscopic ratio $g \approx 2$. This peak is assigned to recombination of non-geminate electron-hole pairs while a much weaker and broader spectrum spread over a width of 130 mT is the signature of localized polymer TEs (see Supporting Information Figure S6). This triplet spectrum is comparable to the optically detected magnetic resonance triplet band in PPVs,^[34–36] but with slightly larger width. The TEs in pristine SY-PPV device are formed by direct ISC from the SEs. The ISC rate in PPV polymers is generally very low,^[43,44] resulting in low EDMR intensities for the TEs in the SY-PPV devices.

Photo-EDMR spectra of SY-PPV:fullerene devices of low fullerene concentration consist of a sharp central peak attributed in this case to bimolecular recombination of CT pairs (and of non-geminate electron-hole pairs inside the domains of the constituting materials). In addition, there is a weak and broad signal assigned to TEs in SY-PPV and a relatively intense and narrower signal of the fullerene TEs (see also Supporting Information Figure S7). TEs in PC(70)BM, and ICBA have significantly narrower EDMR signatures than in the polymers with widths of 26 mT, 32 mT, and 20 mT, respectively, corresponding well with spectra observed in pristine fullerene films.^[45,46] The fullerene TE EDMR signatures are intense relative to those of the polymer TEs due to the high ISC rates in fullerene

Figure 5. EPR spectra ($T = 3.2$ K) measured via photocurrent at zero bias of BHJ devices with different blend ratios for a) SY-PPV:PCBM, b) SY-PPV:PC70BM, and c) SY-PPV:ICBA. Samples are photoexcited at 2.77 eV ($\lambda_{\text{laser}} = 447$ nm). The sharp central peak is due to bimolecular recombination of charges in each blend component, and/or across their interface. The broader features originate from TEs in the fullerene domains.

molecules.^[47] The spectra are visible up to $T = 150$ K, becoming harder to detect because of increasing spin-lattice relaxation at higher temperature. EPR spectroscopy allows, for the first time to the best of our knowledge, the unambiguous demonstration of fullerene triplet production in BHJ polymer:fullerene devices.

In SY-PPV:fullerene devices with high fullerene concentration, the EPR triplet signature of SY-PPV vanishes while those of fullerenes also decrease in intensity. The disappearance of the signal of SY-PPV TEs implies that the polymer triplets observed in devices of low fullerene concentration are produced by direct ISC from SEs. The reduction in EPR intensity of the fullerene TEs, particularly in SY-PPV:PC(70)BM devices, despite increase in fullerene concentration indicates increasing dissociation rate of SEs both in the polymer and fullerene at the interface. At the same time, the limited reduction in intensity of the ICBA TEs EPR signature in SY-PPV:ICBA devices with ICBA concentration confirms the minimal role of interfacial CT states play in charge separation in these devices.

To identify the precursors of the fullerene TEs and the corresponding formation pathways, SY-PPV(50:50)PC70BM and SY-PPV(50:50)ICBA devices are selectively excited using lasers of different energies as shown in **Figure 6**. Under above bandgap excitation, as we discuss above, EPR signatures of TEs in PC(70)BM and ICBA domains have been recorded. Since the intensity of the fullerene TE EPR signature is stronger at low concentration of fullerene (see **Figure 5**) the polymer excitation must contribute strongly toward the fullerene TEs formation. Photoexcitation of the blend devices at 1.89 eV ($\lambda_{\text{laser}} = 655$ nm), which is well below the bandgap of SY-PPV, shows the EPR TE signatures of both PC70BM and ICBA. These TEs could be formed by direct ISC from SEs in the fullerene or direct CT-TE transition. However, when the

low lying CT states (or CT states in the very tail of the distribution in the case of ICBA blend) are directly photoexcited at 1.53 eV ($\lambda_{\text{laser}} = 808$ nm), only the narrow central peak is detected, and no fullerene TE EPR signatures are observed. This unambiguously confirms that the fullerene TEs are produced by ISC from the corresponding SEs. The latter could in turn be produced either by direct above bandgap excitation of the fullerenes, by ET from SEs in SY-PPV, or by high energy CT pair conversion.

2.5. Energy of the Charge Transfer State and Triplet Formation Pathways

The E_T of fullerenes is reported to be ≈ 1.50 eV above the ground state^[22] energetically below the E_T level of SY-PPV ≈ 1.6 eV.^[48] As confirmed by EL measurement, at low PC(70)BM concentration a scanty populated CT state is indeed present in SY-PPV:PC(70)BM. The E_{CT} , defined by the PL peak of the CT emission, is at such low concentration higher than the 1.52 eV determined for SY-PPV(20:80)PC(70)BM. High ISC rate in fullerene, and lack of appreciable charge dissociation probability means that energy transferred SEs are likely to be converted to TEs, which are the lowest excited states (see **Figure 7a**). Our steady state PL study in SY-PPV:fullerene blend films of low fullerene concentration reveals that not all SEs in SY-PPV are quenched. Some of the residual SEs in SY-PPV can be converted to TEs by direct ISC. TEs in SY-PPV near the enclosed fullerenes could be converted to fullerene TEs by Dexter type energy transfer, a process reported in a number of host-guest blends,^[49–52,54] polymer:fullerene blends of low fullerene concentration,^[53] and polymer-polymer blend films.^[33,56] Our EPR detection of TE signature of SY-PPV in these devices of low fullerene

Figure 6. Photo-EDMR spectra ($T = 3.2$ K) of BHJ blend devices normalized for the central peak with a) SY-PPV(50:50)PC70BM and b) SY-PPV(50:50)ICBA detected at different excitation photon energies. While the EDMR signatures of TEs clearly appear in both blends for excitation above either polymer (2.77 eV) or fullerene bandgap (1.89 eV), only the central sharp peak is observed for 1.53 eV excitation.

concentration shows that the TE-TE energy transfer does not completely quench the polymer TEs.

In SY-PPV:PC(70)BM devices of high fullerene concentration, the two materials form interpenetrating networks that facilitate transport of the separated charges from the interface to the electrodes (see Supporting Information Figure S5 for comparison of I - V curves). The strong SY-PPV PL quenching is a result of competitive interfacial charge and energy transfer processes. When the fullerene E_T is energetically below E_{CT} it is clear that ET to the fullerene component acts as a charge-loss process, taking into account the high ISC rate in fullerene compared to the polymer. This actually remains true even if $E_T \geq E_{CT}$, and fullerene TEs can relax to the CT state.^[57] The lower TE energy compared to SE means that lower CT states are populated which possess lower interfacial quantum efficiency for charge separation.^[58] In all SY-PPV:ICBA devices where the CT states are effectively silent for charge separation, the majority of SEs in ICBA are produced by ET and CT mediated SE transfer from SY-PPV. TEs in ICBA are subsequently produced by direct ISC. Figure 7b,c summarize the channels that lead to fullerene TE formation in high concentration SY-PPV:fullerene blend device upon above-bandgap photoexcitation.

In order to characterize the film morphology, atomic force microscopy (AFM) measurements were performed in the whole range of blend ratios for the different fullerenes (see Supporting Information Figure S8) without any indication of domain formation or phase separation. However, differences in morphology, including molecular organization at small length scales and buried structures,^[70] that are not observable in AFM images can have significant influence on the energy of the CT state and the width of its distribution. It is already reported that the energy of interfacial CT states is tuned by the local surrounding, giving it a broad energy distribution of width

0.2–0.4 eV.^[8,59,60] Faist et al. observed EL activation of SEs in one of the components of polymer:fullerene blend devices when E_{CT} is lower than the energy of the singlet by ≈ 0.35 eV or less.^[61] It is also evident from our PL and EL measurements that higher states in the CT manifold in SY-PPV:PC(70)BM blends match in energy with the SE states in PC(70)BM, despite E_{CT} is ≈ 0.2 eV lower than the singlet energy in PC(70)BM. Therefore, this overlap can activate a swift SE transfer, instead of charge transfer, across the interface. This undesirable process will have a negative repercussion on photocurrent (J_{sc}) if the energetic alignment is significant. Such an alignment also means that higher excitations in the CT manifold can populate fullerene TEs via the fullerene SEs.

In light of the above discussion, pushing the V_{oc} of BHJ polymer:fullerene devices close to or beyond 1.0 V, employing indene-C60-multi-adduct or endohedral metallofullerenes, moves E_{CT} closer to or beyond the energy of the singlet state of the fullerene material.^[55] In particular, this CT-SE energy alignment not only activates SE transfer from polymer to fullerene, it also prohibits SEs in fullerene domain from relaxing to the interfacial CT state and contributing to J_{sc} . Except in a few cases of BHJ solar cells based on polythiophene families with high HOMO levels,^[62–64] the gain in V_{oc} using ICBA as an acceptor is outdone by a simultaneous drastic loss in J_{sc} . Therefore, this methodology could improve V_{oc} without activating CT-SE energy alignment only if E_{CT} remains sufficiently below the energy of the lowest singlet states. It is of interest to consider the analogous situation in low bandgap polymer:fullerene solar cells with E_{CT} close to the polymer optical bandgap. In this case, CT states with energy at or above the polymer singlet state become inadequate for relaxation of the polymer SEs at the polymer:fullerene interface. Weak polymer PL quenching in optimized BHJ blend films of low bandgap polymer:fullerene

Figure 7. The Jablonski diagrams for a) SY-PPV:fullerene devices at low fullerene concentration and b) SY-PPV:PC(70)BM and c) SY-PPV:ICBA BHJ devices at high fullerene concentration, focusing on pathways important for TE formation (e.g., SE recombination pathways are not explicitly included). Solid lines represent ISC or CT-mediated SE transfer while broken lines are energy transfer processes. Direct above bandgap photoexcitation both in SY-PPV and fullerene components are assumed at high concentration. Fullerene SE generation from direct photoexcitation of fullerenes in blend films/devices of low fullerene concentration is neglected. Excited state energies defined relative to ground state energy (G_0). For the triplet states, only one of the spin configurations is shown.

may be a symptom of the energetic alignment of CT with polymer singlet state.

Finally, recent reports indicate that reasonable J_{sc} combined with $V_{oc} \geq 1.0$ V can be obtained in BHJ polymer:PC(70)BM solar cell devices^[65,66] using proper additives. Employing the empirical relation between V_{oc} and E_{CT} derived by Veldman et al.,^[67] the E_{CT} in these devices is ≈ 1.5 eV. It would be of interest to measure EL or PL to check whether the undesirable CT-SE energetic alignment has been activated in these devices. The additive may have a role not only in improving the interfacial morphology as discussed in the papers, but also in minimizing the CT-SE alignment by lowering E_{CT} or narrowing its distribution.

3. Conclusions

In summary, our investigation of the interfacial photophysics in SY-PPV:fullerene devices at different composition using complementary optoelectrical and magnetic resonance techniques unambiguously identified both CT and TE formation pathways. Photoexcitation of the optically active layers of these devices produce SEs in the polymer and, to some extent, in the fullerene domains. In devices of low fullerene concentration, where the CT states are ineffective for charge separation, most of SEs in SY-PPV transfer to SEs in the fullerene by energy transfer. TEs both in SY-PPV and fullerene components are formed by direct ISC from their respective SEs. It is not excluded that TE-TE energy transfer also contributes to population of the low

lying fullerene TEs. In BHJ devices of high fullerene concentration, where SEs in SY-PPV are effectively quenched, fullerene TEs are formed from SEs in the fullerene domains by ISC. The latter are formed by ET from SY-PPV, direct photoexcitation, or CT-SE transfer. Although direct CT-TE transition is energetically feasible in these systems, it is kinetically severely suppressed as confirmed by the EDMR measurements when the CT states are directly photoexcited. However, high energy CT states in the CT manifold may contribute to populate the fullerene triplet state indirectly via the SEs. This pathway can severely affect the J_{sc} if the CT-SE energetic alignment occurs over a wide energy range. Provided the energetic alignment is minimized and other factors remain constant, both V_{oc} and J_{sc} could simultaneously be improved toward higher power conversion efficiency by employing fullerene acceptors with high LUMO levels.

4. Experimental Section

Materials: SY-PPV was purchased from Merck, the three fullerene derivatives PCBM, PC70BM, and ICBA were purchased from Solenne. All materials were used as delivered.

Device Fabrication: SY-PPV:fullerene devices were fabricated on patterned ITO coated glass substrates (resistivity = 15 Ω /sq) which were cleaned in ultrasonic bath in acetone for 15 min, then washed in detergent. A second ultrasonic bath in isopropanol for 15 min was followed by ozone treatment for 30 min. The SY-PPV and fullerene derivatives were separately dissolved in chlorobenzene at 60 $^{\circ}$ C overnight (6 mg mL⁻¹ each) and were then mixed with volume fractions of the fullerene solution of 0%, 1%, 3%, 10%, 20%, 50%, and 80%,

leading to the corresponding fullerene w/w ratios. The solutions were heated at 80 °C for 30 min just prior to spin coating. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) dissolved in chlorobenzene was spin coated on top of the glass substrate at 3000 rev min⁻¹ for 2 min, followed by annealing at 100 °C for 15 min to remove residual solvent. The blend SY-PPV: fullerene solutions were spin coated at 1200 rev min⁻¹ (0%, 1%, 3%, 10%, 20% blends), at 450 rev min⁻¹ (50% blends), and at 400 rev/min (80% blends) for 1 min giving active layer thickness between 90–100 nm. The LiF/Al top electrode was deposited in a vacuum chamber at a base pressure of less than 10⁻⁶ mbar.

Optical Film Preparation: Optical films for PL measurements were prepared from the same solutions used for device fabrication with identical spin coating parameters. Films were casted on cleaned glass substrates.

Absorption Spectroscopy: UV–visible absorption measurements of the films were performed in a Varian CARY 500 spectrophotometer applying appropriate background subtraction.

Photoluminescence Spectra: Measurement were performed in a homemade PL set-up based on a 25 cm spectrograph and a linear CCD detector (Toshiba TCD1304DG). Excitation was performed using the focused output of solid state lasers at photon energies 2.77 eV, and 1.89 eV and typical power of 3–6 mW on the sample. Appropriate optical filters were used to block excitation light. The PL spectra were corrected for detector background and instrumental sensitivity. During experiments the samples were held at room temperature in dry nitrogen atmosphere.

Electroluminescence Spectra: The EL setup consisted of a spectrograph (Newport MS260i) and back-illuminated CCD (Andor DV420-BV). During measurements the samples were kept at room temperature in a nitrogen-filled container with a transparent quartz window. The spectra were corrected for instrumental sensitivity.

Time-Resolved Photoluminescence: Time-resolved PL (TR-PL) spectra were obtained by streak camera detection (Hamamatsu Streakscope, 50 ps resolution) after excitation with 400 nm laser pulses (repetition rate 82 MHz, pulse width < 2 ps) from the frequency-doubled output of a Ti-sapphire mode-locked laser (Spectra Physics). Typical power on the sample was 20 μW. Detection of the PL decay at each photon energy was performed with a window of ≈70 nm centered at the nominal wavelength, giving an integrated PL intensity as a function of time. The experiment was performed at room temperature and with the sample mounted in vacuum.

Electrically Detected Magnetic Resonance: EDMR measurements were performed on BHJ polymer:fullerene devices (active area ≈ 12.0 mm² each) fabricated on patterned ITO coated glass substrates (3 cm × 3 cm). The latter were pre-engraved from the backside to permit breaking between the devices that can this way be separately mounted on a holder that allows optical access to the active area of the devices. Electrical connection was maintained by connecting two external wires embedded on the holder to the ITO and LiF/Al electrodes of the device using silver paste. For EDMR measurement, a device mounted on the holder was placed at the center of a rectangular TE102 resonator with optical access of a CW X-band EPR spectrometer (Bruker ESP300E, ≈9.44 GHz). The device was then connected in series with an external load resistor and a Keithley 2004 source meter. The change in current (EDMR signal) through the device was detected via the voltage change (ΔV) across the external load resistor (R) when magnetic resonance conditions were satisfied inside the resonator. The resonant change in photocurrent (ΔI_{sc}) through the device was calculated from ΔV/R, which was then normalized by the off-resonance current, I. High signal to noise ratio was reached using an external lock-in amplifier connected in parallel with R. The EPR instrument was equipped with a helium flow cryostat (Oxford Instrument Inc.) for low temperature measurements (T = 2.4–300 K).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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