Sub-ns triplet state formation by non-geminate recombination in PSBTBT:PC$_{70}$BM and PCPDTBT:PC$_{60}$BM organic solar cells†

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The solid-state morphology and photo-generated charge carrier dynamics in low-bandgap polymer:fullerene bulk heterojunction photovoltaic blends using the donor–acceptor type copolymers PCPDTBT or its silicon-substituted analogue PSBTBT as donors are compared by two-dimensional (2D) solid-state nuclear magnetic resonance (NMR) and femto- to microsecond broadband Vis-NIR transient absorption (TA) pump–probe spectroscopy. The 2D solid-state NMR experiments demonstrate that the film morphology of PCPDTBT:PC$_{60}$BM blends processed with additives such as octanedithiol (ODT) are similar to those of PSBTBT:PC$_{60}$BM blends in terms of crystallinity, phase segregation, and interfacial contacts. The TA experiments and analysis of the TA data by multivariate curve resolution (MCR) reveal that after exciton dissociation and free charge formation, fast sub-nanosecond non-geminate recombination occurs which leads to a substantial population of the polymer's triplet state. The extent to which triplet states are formed depends on the initial concentration of free charges, which itself is controlled by the microstructure of the blend, especially in case of PCPDTBT:PC$_{60}$BM. Interestingly, PSBTBT:PC$_{70}$BM blends show a higher charge generation efficiency, but less triplet state formation at similar free charge carrier concentrations. This indicates that the solid-state morphology and interfacial structures of PSBTBT:PC$_{70}$BM blends reduces non-geminate recombination, leading to superior device performance compared to optimized PCPDTBT:PC$_{60}$BM blends.

Broader context

The growing demand of electrical power paired with the limited abundance of fossil energy sources steadily increases the importance of alternative and sustainable energy sources such as solar power. In this respect a very promising technology is organic photovoltaics, since large area devices can be produced at low costs. While in the first generation of organic photovoltaic materials the absorption was mostly limited to the visible part of the solar spectrum thereby significantly limiting the solar photon harvesting, the development of novel donor–acceptor type materials has recently pushed efficiencies towards 10%. However, many of the novel low-bandgap systems underperform as additional loss channels such as triplet state formation exist. Sophisticated transient spectroscopy studies paired with advanced data analysis methods can help to unravel these loss processes and to develop meaningful structure–property relations for a more guided material design. In fact, a careful control of interfacial and bulk morphology appears to be essential to suppress these undesired loss channels.

Introduction

The past years have witnessed a steady increase of the power conversion efficiency (PCE) of solution-processed organic solar cells now reaching 9% PCE for single junction photovoltaic devices and even exceeding 10% PCE for tandem solar cells. The substantial improvement during the last years was in part a consequence of the development of novel low-bandgap polymers, covering a broader spectral range of the solar photon flux compared to mid-bandgap polymers such as the heavily researched polymer regioregular poly(3-hexylthiophene). The alternating
donor–acceptor (D–A) copolymers poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and poly[[4,4’-bis(2-ethylhexyl)dithieno[3,2-b:2’,3’-d:5,6]dithieno[2,1,5-bf:3’,4’-cd]silole]-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT) are prototypes of such low-bandgap polymers with an onset of photocurrent generation beyond 500 nm. The chemical structure of the two copolymers is very similar, where the only difference between them is that the bridgehead carbon atom (where the solubilizing side chains are attached) in PCPDTBT is substituted by a silicon atom in PSBTBT. Both polymers have attracted much attention as electron donor material in photovoltaic blends with [6,6]-phenyl C70-butyric acid methyl ester (PC70BM) as acceptor, reaching PCEs around 5%. However, the highest PCE for PCPDTBT could only be reached when using high boiling point cosolvents, such as octanediol (ODT) or 1,8-diodo-octane (DIO), during film preparation. The cosolvents cause partial demixing of the blend’s components and create larger polymer-rich domains with increased order thereby facilitating charge separation, transport, and extraction. Interestingly, for PSBTBT:PCBM, a cosolvent is not necessary to achieve optimum device performance as the silicon-substitution has a significant impact on the morphology of the blend, which in fact is similar to the effect of solvent additives on the morphology of PCPDTBT:PCBM blend films. Several previous studies have addressed the origin of the increased performance of PSBTBT:PCBM compared to PCPDTBT:PCBM. Hou et al. reported a three times higher hole mobility in pristine PSBTBT compared to pristine PCPDTBT in organic field effect transistors (OFETs). According to Chen et al., the increase in hole mobility is caused by improved \( \pi-\pi \) stacking due to the larger bond length of the C–Si bond in PSBTBT compared to the C–C bond in PCPDTBT. The greater bond length was shown to reduce steric hindrance from the bulky alkyl sidechains thereby leading to increased semicrystallinity for PSBTBT compared to the largely amorphous PCPDTBT. Similar explanations were put forward by Morana et al., who used X-ray diffraction (XRD) to show improved \( \pi-\pi \) stacking. The authors further reported a higher charge photogeneration yield for PSBTBT:PCBM blends and correlated this property with a reduction of charge-transfer (CT) state formation and recombination at the interface. Guibert et al. investigated the influence of the bridgehead atom by wide-angle X-ray scattering and molecular modeling and found that the substitution of the carbon atom by a silicon atom led to a decreased \( \pi-\pi \) stacking distance in conjunction with an increased lamellar stacking distance.

Very recently, Rao et al. reported that non-geminate recombination leads to the formation of polymer triplet states in the low-bandgap polymer:fullerene system PCPDTBT:PC70BM, which in turn strongly affects the device performance. Recent results by Chow et al. further revealed that upon addition of ODT triplet generation was promoted due to increased generation of free charges. A limitation of the device performance by triplet state generation in PCPDTBT:PCBM was also proposed by Di Nuzzo et al., while Distler et al. recently extended the quasi-steady state photo-induced absorption (cw-PIA) studies reported previously to PSBTBT:PC70BM blends for which they demonstrated negligible triplet generation. However, cw-PIA measurements do not accurately capture generation and recombination processes, as the technique measures lifetime and concentration-averaged photo-induced absorption signals, and therefore the role of triplet states in PSBTBT:PCBM photovoltaic blends still remains unclear. In fact, compared to PCPDTBT:PCBM blends, where enhanced triplet generation has been observed in optimized morphologies created by adding the cosolvent ODT, it is yet unknown how the substitution of the carbon bridgehead atom by silicon affects the photophysical processes in a solar cell. Specifically, this involves the charge generation, formation of triplet states, and excited state dynamics in comparison to the carbon-bridged analogue PCPDTBT. Only very recently Tamai et al. reported transient absorption (TA) experiments on PSBTBT:PCBM blends, covering the Vis-NIR spectral range and ps-μs dynamic range. The authors concluded that exciton dissociation is in part diffusion-limited and they could distinguish between hole polarons in disordered (amorphous) and semicrystalline polymer domains on the basis of their different spectral signatures. They also found that the former are prone to sub-nanosecond geminate recombination, while the latter are longer-lived and contribute to the photocurrent. Hole transfer from disordered to ordered domains was also observed, however, triplet state formation was not reported in their study.

Here, we investigated the solid-state morphology and charge generation and recombination processes in PSBTBT:PCBM blends by solid-state NMR and transient absorption pump–probe spectroscopy, respectively, and compared the results to those recently obtained on PCPDTBT:PCBM and PSBTBT:PCBM blends by others and us. Specifically, we address the origin for the performance increase observed if PSBTBT is used instead of PCPDTBT in a photovoltaic blend. We demonstrate by soft-modeling of the experimentally obtained TA data, namely by multivariate curve resolution alternating least squares (MCR-ALS) analysis, that triplet state formation by fast sub-nanosecond non-geminate recombination constitutes a loss channel in PCPDTBT:PCBM blends prepared with ODT, whereas this loss channel is significantly reduced in the PSBTBT:PCBM blend in part explaining the much higher device performance of the latter.

**Experimental**

**Materials**

The PCPDTBT polymer used in the present study was obtained from 1-material Organic Nano Electronic and used as received. The molecular weight of the polymer was \( M_n = 14,000 \text{ g mol}^{-1} \). PSBTBT was purchased from Konarka with a molecular weight of \( M_n = 16,000 \text{ g mol}^{-1} \) and a polydispersity of 3.72 and was also used as received. We determined the molecular weights in-house using hot GPC with trichlorobenzene at 80 °C as eluent and referenced against polystyrene standards.

**Sample preparation**

The solar cells were processed on ITO-covered glass substrates (Präzisons Glas & Optik GmbH, Germany) patterned by wet
etching. On top of the ITO a PEDOT:PSS layer was spin-cast from aqueous solution at 3000 rpm in 60 s and afterwards dried in a glovebox at 150 °C for 10 minutes. Above that the active layer was spin-cast followed by the evaporation of a 10 nm calcium and a 100 nm aluminum electrode. For the preparation of PCPDTBT: PC60BM blends, both materials were dissolved together in ratio of 1:2 with a polymer concentration of 10 mg ml⁻¹ in chlorobenzene or a chlorobenzene ODT mixture containing 3 vol% of ODT. The solution was spun-cast at 80 °C at 1400 rpm for 40 s. PSBTBT: PC70BM samples were spin-cast from a dichlorobenzene solution in ratio of 1:1.5 with a polymer concentration of 14 mg ml⁻¹ at 1400 rpm for 40 s at 70 °C.

Samples used for optical spectroscopy were spin-cast on cleaned quartz substrates with the same conditions as for solar cell preparation. For experiments on polymer: triplet sensitizer films, 40 wt% of PtOEP was used. Samples for solid-state NMR spectroscopy were dropcast on glass substrates from different solvents indicated in the main text and dried for several days in the glovebox. Subsequent application of vacuum was used to remove residual solvents. Afterwards, the polymer film was scratched from the glass substrate and transferred into an NMR rotor.

**Solid-state NMR spectroscopy**

Solid-state magic-angle spinning (MAS) NMR experiments were carried out on a Bruker Avance III spectrometer operating at 20.0 T (νH = 850.27 MHz for 1H, νC = 213.82 MHz for 13C) using a commercial 2.5 mm double resonance probe (Bruker). 1D 13C MAS NMR spectra used for assignment purposes (see Fig. S1, ESI†) were obtained through 13C{1H} cross-polarization (CP) at a spinning frequency of 25.0 kHz with a repetition delay of 2 s and a total number of scans varying from 24,576 to 49,152, depending on the available amount of sample. 2D 13C{1H} frequency switched Lee-Goldburg (FSLG) heteronuclear correlation (HETCOR) NMR spectra were recorded at a spinning frequency of 15.0 kHz using a repetition delay of 2 s and a number of scans varying from 896 and 2176 for a total of the 40 r1 increments. The 2D experiments employed LG-CP conditions to suppress 1H spin diffusion during CP. For all 1D and 2D NMR experiments the specific CP and LG-CP conditions, respectively, were preoptimized on L-alanine. The CP contact time was set to 3.0 ms for all experiments and two-pulse phase modulation (TPPM) high-power 1H decoupling was applied during acquisition. All spectra were referenced to adamantane as a secondary standard (δiso = 1.85 ppm for 1H, δiso = 38.484 for 13C). Identical processing conditions were used for all 1D and 2D NMR spectra. All 2D NMR spectra were plotted on the same intensity scale with 12 contour lines from 5.0 to 99.0% of the maximum intensity using the commercial tospin software (Bruker).

**Results**

**Blend morphology**

The blend morphology of PSBTBT:PC60BM blends in terms of local molecular order and interfacial structure was investigated by solid-state NMR spectroscopy and compared to the NMR results that we recently obtained on PCPDTBT:PC60BM blends. Using this technique we utilize the fact that the isotropic 13C NMR line width, obtained under fast magic-angle spinning (MAS), reflects the distribution of local site geometries and thereby, the average degree of ordering at the molecular level. A further advantage of solid-state NMR is its ability to probe the spatial proximity of chemical groups on the sub-nanometer scale via through-space dipole–dipole coupling between nuclear spins. Thus, the combination of 13C chemical shift information combined with two-dimensional (2D) 13C dipolar-mediated heteronuclear correlation (HETCOR) NMR is a powerful approach for studying molecular packing and heterogeneities in addition to spatial arrangements of molecular entities.

Fig. 1b–d summarize the 2D solid-state 13C{1H} FSLG-HETCOR NMR spectra of PCPDTBT:PC60BM and PSBTBT:PC60BM blends both drop-cast from o-DCB and, in the case of PCPDTBT:PC60BM, also from o-DCB containing 2.44% (vol%) ODT as a solvent-additive. PCPDTBT:PC60BM obtained from dissolution in pure o-DCB exhibited the broadest 13C signals of all blends (Fig. 1b).
and thus, the lowest degree of local molecular ordering. Processing the same material with ODT resulted in an increased molecular order, as indicated by the narrower $^{13}$C line widths in the aliphatic region (10–60 ppm), which is even more pronounced for the aromatic $^{13}$C signals in the 110–160 ppm region (Fig. 1c). We note that similar effects concerning local molecular order have recently been reported for pure PSBTBT when addressing the effects of thermal annealing. Nevertheless, the PSBTBT:PC$_{60}$BM blend showed most narrow $^{13}$C line widths and thereby the highest average local ordering of all samples even without addition of ODT to the solution (Fig. 1d).

The aliphatic resonance highlighted in green in the 2D $^{13}$C{$_{1}$H} FSLG-HETCOR NMR spectrum of PCPDTBT:PC$_{60}$BM drop-cast from o-DCB (Fig. 1b) can be unambiguously assigned to the methylene group (C6) next to the bridgehead carbon atom of the 2-ethylhexyl side chains (see Fig. 1a and Fig. S1, ESI†). The absence of this $^{1}$H–$^{13}$C heteronuclear correlation after processing PCPDTBT:PC$_{60}$BM with ODT (Fig. 1c) suggest changes in the 2-ethylhexyl side chain conformation. The absence or strong intensity reduction for the C6 signal is likely due to an interference between the local molecular mobility of the CH$_{2}$ group and the time scale of the NMR experiment as has been observed in recent solid-state NMR studies as well. This interference leads to a signal loss and possible broadening when the frequency of the associated motion is matched by the frequency of either (i) the involved $^{1}$H–$^{13}$C dipole–dipole couplings, (ii) the proton decoupling/cross-polarization fields, or (iii) the magic-angle spinning. Thus, this difference between the two blends is most likely related to a spatially more favorable 2-ethylhexyl side-chain arrangement for PCPDTBT:PC$_{60}$BM processed with ODT. These observations are in agreement with literature reports showing that ODT acts as a small-molecule plasticizer for PCPDTBT:PC$_{60}$BM blends, amorphous polymer: fullerene systems and also small molecules.

For PSBTBT, the replacement of the bridgehead carbon atom by silicon (Fig. 1d) leads to a new correlation signal located at $\delta_{\text{iso}}$(13C) ~ 20 ppm (highlighted in green, filled rectangle). This signal can be assigned to the methylene group (C6) of PSBTBT (see Fig. 1 and Fig. S1, ESI†). The characteristic shift to lower 13C chemical shift (or equivalent higher field) is not only caused by the change in chemical nature of the bridgehead atom, but also comes as a result of changes in bond lengths and angles around the silicon atom compared to its carbon analogue as shown in a recent study. This study
Thus, the blends of PCPDTBT:PC60BM processed with ODT and NMR spectrum of PSBTBT processed without ODT (Fig. 1d). Similarly, these correlation signals are absent in the 2D 13C{1H} FSLG-HETCOR NMR spectrum (Fig. 1c). Likewise, these correlations can be assigned to intramolecular 1H-13C pairs of aliphatic and aromatic functionalities that are either directly bonded or in close proximity to each other. Besides these intrinsic, expected connections, intermolecular contacts between aliphatic-aliphatic and aromatic-aromatic moieties can also contribute to the signal intensity in the aforementioned regions. This includes intermolecular contacts between aliphatic side chains that occur between stacks of PCPDTBT/PSPTBT polymer chains and aromatic-aromatic donor-acceptor contacts, arising from closely stacked PSBTBT and PCPDTBT polymer chains.21 In the 2D 13C{1H} FSLG-HETCOR NMR spectrum of PCPDTBT:PC60BM drop-cast from pure o-DCB (Fig. 1b), additional correlation signals are present between aliphatic 13C and aromatic 1H moieties (highlighted in orange). Such signals can in principle arise from intramolecular contacts caused by back folding of 2-ethylhexyl side chains onto the PCPDTBT backbone or folding of the butyric methyl ester functionalities (handle) onto the fullerene of PCBM. Both scenarios would inhibit the growth of sufficiently large PCPDTBT and PCBM domains, leading to an intimate molecular mixing of the two blend components. Such a scenario is likely to be accompanied by a low PCE due to dominant recombination processes.5d Another possibility is that the mixing of PCPDTBT and PCBM leads to intercalation of the 2-ethylhexyl side chains and butyric methyl ester functionalities between adjacent aromatic moieties as indicated in Fig. 1a. However, processing the PCPDTBT:PC60BM blend with ODT clearly leads to the disappearance of these aliphatic carbon and aromatic proton correlations in the 2D 13C{1H} FSLG-HETCOR NMR spectrum (Fig. 1c). Likewise, these correlation signals are absent in the 2D 13C{1H} FSLG-HETCOR NMR spectrum of PSBTBT processed without ODT (Fig. 1d). Thus, the blends of PCPDTBT:PC60BM processed with ODT and that of PSPTBT:PC60BM both appear to have better defined intra- and intermolecular ordering of the constituents that is accompanied by the formation of larger polymer- and PCBM-rich domains in the blend.5d The improved ordering of both polymer and PCBM and, in particular, the separation of aromatic and aliphatic functionalities, is known to correlate with improved aromatic-aromatic interfaces and enhanced charge transport properties.7,22

Steady-state absorption and photovoltaic performance

Fig. 2a shows the absorption spectra of a PSBTBT:PC70BM (1:1.5) blend, a PCPDTBT:PC60BM (1:2) blend, and a PCPDTBT:PC60BM (1:2) blend processed with the solvent additive ODT. As reported earlier, the addition of ODT to the solution prior to spin-casting the film causes a red-shift of the polymer’s absorption in conjunction with a more pronounced vibronic structure, indicating demixing of the blend’s components and enhanced order of the polymer. The red-shift and vibronic structure are even more pronounced in the PSBTBT blend in line with the enhanced semi-crystallinity reported for this system.5 The absorption difference between 450–600 nm of the PCPDTBT compared to the PSBTBT blends is the result of the additional absorption caused by the C70 fullerene derivative used in the latter blend. PC70BM increased the device performance (see Fig. 2b) due to enhanced harvesting of solar illumination by increasing the photoactive layer’s absorption. As we have recently shown, PCPDTBT:PC60BM devices prepared without ODT have a JSC of 3.8 mA cm−2 and a FF of only 0.38 that result in a low PCE of 1.0%. Addition of ODT to the solution for spin-casting doubled the PCE to 2.2% for PC60BM and 2.7% for PC70BM, respectively, however the FF still remained rather low at 0.45. Solar cells built from PSBTBT:PC60BM show a JSC of 10.4 mA cm−2, and a fill-factor of 0.64 yielding a PCE of 4.6%, which is in good agreement with the efficiencies very recently reported by Di Nuzzo et al.23

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The text is focused on the role of solvent additives (ODT) in improving the performance of solar cell blends, specifically examining the absorption and photovoltaic properties of different blend compositions. The study highlights the importance of intermolecular and intramolecular interactions in determining the performance of these materials, with ODT playing a critical role in enhancing order and separation of functionalities within the blend.
The increase in FF indicates that field-dependent processes are strongly reduced in PSBTBT:PC_{70}BM compared to PCPDTBT:PC_{60}BM. In fact, Albrecht et al. have recently shown that charge generation is strongly field-dependent in PCPDTBT:PC_{70}BM blends, while it is only weakly-field dependent in PSBTBT:PC_{60}BM blends, resulting in a higher $J_{SC}$ and FF of the latter.$^{24}$

**ps–µs excited state dynamics in PSBTBT:PC_{70}BM**

The exciton and charge carrier dynamics in blends of PSBTBT:PC_{70}BM were investigated by broadband Vis-NIR transient absorption (TA) pump–probe spectroscopy covering a dynamic range from pico- to microseconds. Here, we demonstrate that the charge generation dynamics depend on the excitation wavelength and furthermore that after exciton dissociation has been completed and free charge carriers have been created, another excited state is generated in a consecutive process. By applying evolving factor analysis (EFA) and model-free multivariate curve resolution (MCR) on the TA data as recently discussed by us and further explained in the ESI† we extract the minimum number of excited states contributing to the experimentally-determined TA data matrix and the individual spectra and dynamics of all excited states. Finally, by comparison with the separately measured triplet-state induced absorption spectrum we identify the consecutively generated component as the polymer triplet state.

Fig. 3 shows the ps–ns Vis-NIR TA spectra of a PSBTBT:PC_{70}BM blend after excitation of the polymer at 800 nm. The spectra exhibit a positive signal below 800 nm, which we assign to the ground state bleach (GSB) of the polymer, as its spectral position coincides with the ground state absorption. At longer wavelength a broad photoinduced absorption (PA) was observed that reaches further into the NIR spectral region even beyond 1500 nm. Plotting the signal dynamics of the PA between 1450–1500 nm shows that it drops substantially within the first 10 ps after photoexcitation. A comparison with TA spectra of a pristine PSBTBT film (see Fig. S2, ESIF) suggests that the PA in this spectral region is dominated by singlet exciton-induced absorption of the polymer. It appears that upon excitation at 800 nm some excitons are generated in polymer-rich regions of the film and have to diffuse to the interface prior to charge transfer.

In stark contrast to excitation of the polymer at 800 nm, excitation at 530 nm predominantly excites the fullerene-rich regions of the blend. The GSB of the polymer shows a prolonged rise up to a few hundred picoseconds, indicating that the initially created excitons do not reside on the polymer prior to charge transfer, but rather on the fullerene.$^{24}$ In fact, the prolonged rise of the polymer’s bleach in conjunction with a rise of the charge-induced absorption also suggests that diffusion of excitons in the PC_{70}BM domains is rather slow and that fullerene-rich domains are extended in the blend. Furthermore, the dynamics show a pronounced fluence dependence indicating fullerene exciton–exciton and/or exciton–charge annihilation prior to the exciton dissociation at the interface. However, we note that higher order effects are only relevant at excitation densities largely exceeding 1-sun conditions, while they are absent at the lowest fluences used in our TA experiments.

In order to determine how many excited states contribute to the measured TA data matrix, we performed EFA on the PSBTBT:PC_{70}BM blend’s sub-ns TA NIR data for all excitation densities after exclusive excitation of the polymer at 800 nm. At approximately 10 ps, that is, the time required for complete polymer exciton quenching, the TA NIR data can be accurately described by a single component. We assigned this component to charges generated upon exciton dissociation at the interface as commonly observed in polymer-fullerene blends. Surprisingly, at later delay times a second component was clearly revealed by EFA, whose onset shifted to earlier delay times with increasing pump fluence, indicating that its generation is controlled by a fluence-dependent process (see Fig. S3 for EFA plots, ESI†). To determine the associated component spectra and dynamics we applied multivariate curve resolution (MCR) analysis with alternating least squares (ALS), using a matrix factorization algorithm recently developed by Tauler et al.$^{26}$ (see also SI and Fig. S4, ESIF). We note that MCR analysis is a common tool in other spectroscopy communities, for instance, it is used in NMR spectroscopy to separate the individual contributions of components in liquid-state and diffusion ordered spectroscopy (DOSY) NMR spectra$^{27}$ and in HPLC-DAD to identify single components in a multicomponent mixture.$^{28}$ We have recently applied MCR analysis to TA experiments on polymer:perylene diimide blends to unravel the efficiency-limiting processes in these photovoltaic systems.$^{29}$ Here, we determined that three components contribute to the TA data.
matrix on the ps–ns timescale, while it is only two components on the ns–μs timescale. Thus, we first analyzed the ns–μs data as the complexity of the data analysis increases with the number of components. Fig. 4 shows the results of the MCR-ALS analysis of the TA data of PSBTBT:PC70BM on the ns–μs timescale constrained to non-negativity of spectra and concentration profiles.

Interestingly, the spectrum of component 1 that results from the MCR-ALS analysis is virtually the same as the triplet-induced absorption shown in Fig. 4, which we measured on a blend of PSBTBT and the triplet sensitizer platinum octaethylporphyrin (PtOEP), as we have previously also demonstrated for PCPDTBT.5d We fixed the triplet spectrum in the MCR analysis and obtained a set of potential spectra (Fig. S5a, ESI†) and concentration profiles (Fig. S5b, ESI†) for component 2. A comparison of both component spectra obtained by MCR-ALS analysis (see Fig. 4) to the separately measured triplet- and charge-induced absorption spectra confirmed that the ns–μs transient absorption surface of PSBTBT:PC70BM can indeed be very well described by these two states.

Fig. 5 shows the dynamics of triplets and charges for three different excitation densities obtained by factorization of the ns–μs TA surface based on the triplet-induced absorption spectrum and the charge-induced absorption spectrum. The concentration profiles shown in Fig. 5 (Fig. S9 for normalized kinetics, ESI†) clearly demonstrate that charges and triplets exhibit concentration dependent decay dynamics. In case of the charge carriers fluence dependent dynamics point to non-geminate recombination, but in case of the triplet states an exponential decay with an inverse rate of several hundred nanoseconds or even microseconds is expected, if triplets decayed with their intrinsic lifetime. However, the concentration dependence of the triplet dynamics suggests that charge-triplet annihilation and triplet–triplet annihilation occur and dominate the triplet dynamics as recently also demonstrated for PCPDTBT:PC70BM blends.10

To analyze the ps–ns TA data we added the absorption spectrum of the polymer singlet states obtained on a pristine PSBTBT film by TA spectroscopy (see Fig. S2, ESI†) to the data analysis. In fact, using a combination of the charge-induced, triplet-induced, and singlet-induced absorption spectra as input parameters, we were able to uniquely determine the contribution of each species on the ps–ns timescale. Fig. 6 shows the NIR transient absorption data surface of a PSBTBT:PC70BM blend after excitation at 800 nm with a low fluence of 2.9 μJ cm⁻² and depicts the normalized component spectra as obtained by matrix factorization. The respective concentration profiles are shown as well for the three lowest fluences between 1.4–2.9 μJ cm⁻². The concentration profiles
were obtained by matrix division using a cross-section ratio of 
\[ \sigma_{\text{excitons}} = 2.8 \times \sigma_{\text{charges}} \text{ and } \sigma_{\text{triplet}} = 2\sigma_{\text{charges}} \]
the latter which has recently been reported for PCPDTBT:PC_{70}BM, assuming
that the cross section ratio is similar in PSBTBT:PC_{70}BM.\(^{30}\) The
cross-sections of charges and singlet excitons were simply
determined from the TA spectra of the blend at a delay time of
20 ps, that is, at a time when only charges were present in the
blend, and from measurements on a pristine polymer film,
respectively, according to
\[ \sigma_{\text{species}} = \frac{\Delta T / T}{Nd} \]
in which \(\Delta T / T\) is the amplitude of the transient absorption
signal at a chosen delay time, \(N\) the number density of excited
states calculated from the sample’s absorption and excitation
fluence and \(d\) is the film thickness.

The polymer excitons decay in about 10 ps and cause a
concomitant rise of the charge-induced absorption on the same
timescale pointing towards a diffusion-limited exciton dissociation
process as already discussed above. However, a fraction of
charges was already present directly after excitation, indicating
ultrafast charge generation faster than our time resolution of
\(\sim 200\) fs. The rise of the charge-induced absorption continues
up to 10–20 ps and is followed by fluence dependent recombination
(see also Fig. S8 for normalized dynamics, ESI†). The
decay of the charges is correlated with the rise of the population
of polymer triplet states, starting at around 100 ps for the
lowest fluence used in our experiments. We note that the onset
of triplet formation obtained by MCR-ALS analysis is in excellent
agreement with the results obtained by EFA (see above).

**Excited state dynamics in PCPDTBT:PC_{60}BM blends**

In this section we compare the results obtained on the ps–ns
timescale for PSBTBT:PC_{70}BM presented above with data
obtained on PCPDTBT:PC_{60}BM blends prepared with and without
solvent additives. To the best of our knowledge, such an
analysis of the ps–ns dynamics in PCPDTBT:PC_{60}BM has not
been presented yet, while the ns–μs dynamics have been
presented earlier.\(^{10}\)

We note that the device performance of PCPDTBT:PC_{60}BM
blends prepared with and without ODT and PCPDTBT:PC_{70}BM
blends prepared with ODT is significantly worse than that of
PSBTBT:PC_{70}BM blends. In Fig. 2 we compare the \(J–V\) curves of
all systems clearly demonstrating that the performance of the
PCPDTBT:PC_{60}BM and PCPDTBT:PC_{70}BM devices is limited by
the low fill-factor independent of the fullerene derivative used. We
have previously reported the charge generation and recombination
processes in PCPDTBT:PC_{60}BM prepared with and without
ODT and used a simple two-pool model to parameterize the
carrier dynamics.\(^{5d}\) In light of the recent results reported by Chow
et al.\(^{10}\) and our results obtained on PSBTBT:PC_{70}BM blends
shown here, we revisited the data analysis after retaking the
PCPDTBT:PC_{60}BM TA data using an improved NIR TA setup with
enhanced signal to noise ratio. Interestingly, the EFA analysis of
the ps–ns and ns–μs TA data measured for PCPDTBT:PC_{60}BM
indicated, as observed for the PSBTBT:PC_{70}BM system, that after
polymer exciton quenching was completed a second component
in addition to the charge carriers is generated. Applying MCR-ALS
analysis to the TA data obtained on PCPDTBT:PC_{60}BM blends
prepared with ODT revealed that the generation of the second
component is significantly faster in this blend causing its total
concentration to be higher compared to a blend prepared without
ODT. Fig. 7 displays the concentration profiles obtained from the
factorization of the sub-ns TA data of the blend processed without
ODT (a) and processed with ODT (b). In line with the interpreta-
tion of the data on PSBTBT:PC_{70}BM, we identified the second
component as the polymer triplet state by comparison with the
independently measured triplet-induced absorption spectrum
(see ESI†). We note that the triplet as well as the charge-
induced absorption spectra in the blend prepared without ODT
are slightly blue-shifted compared to the PCPDTBT:PC_{60}BM blend
prepared with ODT in good agreement with recent literature
results.\(^{10}\) Furthermore, the generation of triplets is slower in the
former than in the PCPDTBT:PC_{60}BM blend prepared with ODT.
For the PCPDTBT:PC_{60}BM system prepared without ODT the
triplet-induced spectrum obtained by TA measurements on the
pristine polymer is in perfect agreement with the spectrum
obtained by MCR-ALS analysis of the TA data clearly supporting
the assignment of triplet state formation (see Fig. S11, ESI†).\(^{10}\)
Furthermore, we found that the TA spectrum obtained on the

![Fig. 7](image-url)
The temporal evolution of the charge carriers significantly differs for the two blends, showing only a minor decay of approximately 15% on the first two nanoseconds for PSBTBT:PC70BM blends, but a more than 60% decay in the PCPDTBT:PC60BM blends processed with ODT. The fast decay of charges in the latter is accompanied by a fast rise of the triplet population in contrast to PSBTBT:PC70BM blends, in which the onset of triplet formation is approximately at 100 ps.

**Discussion**

Our TA measurements and data analyses revealed that after exciton dissociation and charge transfer is completed another excited state is generated. The presence and rise of this additional component besides the formation of free charges was indicated by evolving factor analysis. Successive MCR-ALS analysis of the TA datasets allowed us to determine the component spectra and their dynamics. Comparison of the component spectra to independently obtained absorption spectra of singlet and triplet excitons as well as charges allowed to identify the presence of these states and their dynamics in the ps–ns and ns–μs time region. However, it is not straightforward to pin down the mechanism behind the formation of triplet states. The fluence dependence of the onset of triplet state formation corresponding to the rise of the triplet-induced absorption plus the observation of enhanced triplet state formation upon more efficient free charge carrier formation in the PCPDTBT:PCBM blends implies that they are generated by non-geminate recombination of free charge carriers as very recently also suggested by Rao et al. and Chow et al.9,10 In fact, when two oppositely charged free carriers encounter at the donor–acceptor interface, they may create a loosely-bound charge transfer state across the interface prior to recombination.31,32 Since the electron spins of the free charge carriers are initially uncorrelated, simple spin statistics determines that three quarters of the interfacial states should be spin triplets, while one quarter is expected to be singlets, very much alike the recombination of free charges injected from electrodes in organic light-emitting diodes (OLEDs). However, the interfacial CT states created upon free charge recombination can re-dissociate into free charges, spin flip from the singlet to the triplet or vice versa, or recombine controlled by the kinetics of these processes as suggested by Rao et al.9 Alternatively, triplet formation could occur via intersystem crossing of CT states immediately created after singlet exciton dissociation.33 However, recent measurements on PCPDTBT:PC60BM and PSBTBT:PC60BM blends revealed a lifetime of these CT states of a few hundred picoseconds only,11,14 which appears to be too short to create a substantial yield of triplets by intersystem crossing (ISC).

The population of polymer triplet states occurs, if the triplet state of the polymer is lower in energy than the interfacial triplet CT state, causing a downhill energy transfer process, which competes with re-dissociation of the CT state. This process adds another loss channel to the efficiency-limiting processes in organic solar cells, and hence likely decreases its efficiency. Fig. 9 sketches an overview of the possible processes in the investigated polymer:fullerene bulk heterojunction blends.

A comparison of the PSBTBT:PC70BM blend and the PCPDTBT:PC60BM blend prepared with ODT revealed that the triplet generation in the latter was significantly enhanced.
We note that our TA measurements were conducted on blend films without any electrodes, that is, in the absence of any electric field, corresponding to open-circuit conditions in a solar cell. Hence, all photogenerated charge carriers are forced to eventually recombine to the ground state. Due to the higher charge carrier mobility in PSBTBT compared to PC70BM, the yield of triplets was small in PSBTBT:PC70BM blends and supports that they are created by non-geminate recombination. The free charge carrier density of a solar cell is expected to be faster in the former and thus enhanced triplet formation is expected, but interestingly not observed. This points to a suppression of triplet generation in PSBTBT:PC60BM blends.

Does triplet state formation by non-geminate recombination play a role for the photovoltaic performance at one-sun illumination conditions? In our TA experiments the lowest charge carrier density at which we could still achieve a reasonable signal-to-noise ratio was around $2 \times 10^{17}$ cm$^{-3}$. Chow et al. performed TA experiments at even smaller carrier densities between $10^{16}$ and $10^{17}$ cm$^{-3}$, which explains the slower triplet generation observed in their experiments and supports that they are created by non-geminate recombination of free charges. The free charge carrier density of a solar cell operated at open-circuit conditions was determined to be between $10^{16}$ and $10^{17}$ cm$^{-3}$ by Credgington et al. using a charge extraction experiment. This implies that our lowest excitation densities were close to solar operating conditions and thus, the effects observed in our experiments could indeed play a role for the photovoltaic performance.

However, the quantitative analysis of the generation and recombination rates is difficult as the absolute cross-sections of the invoked excited states are unknown. Nevertheless, some conclusions regarding the device performance can be drawn from the blend’s IQE estimated from the EQE measurements and the film absorption following the approach recently published by Burkhard et al. In the case of PSBTBT:PC70BM, we obtained a maximum IQE of 73%, which is in excellent agreement with measurements recently presented by Albrecht et al. This implies that about 30% of the initial photoexcitations are somehow lost in PSBTBT:PC70BM. The comparably high fill-factor of the photovoltaic devices further indicates that losses

![Diagram of proposed photophysical processes in low-bandgap polymer:fullerene solar cells.](Image)
are mainly due to field-independent processes and that charge generation was only weakly field-dependent. In contrast in PCPDTBT:PC60BM blends prepared with ODT the maximum IQE was determined to 52%. The lower IQE and fill-factor of the devices (see Fig. 2) point to faster non-geminate recombination, which is in good agreement with the high triplet generation yield. Due to the early (sub-100 ps) onset of non-geminate recombination, a meaningful quantification of the geminate losses in this material system was difficult. However, literature reports confirm that geminate recombination in PCPDTBT:PC60BM prepared with ODT is reduced compared to the blend prepared without ODT. In fact, for the latter a much lower IQE of only 28% was calculated. We note that in our previous study of the photophysics of PCPDTBT:PC60BM we determined the amount of geminate recombination from the decay of the ground state bleach on the first 10 ns based on the assumption that non-geminate recombination did not play a role on this time scale. This is true for the lowest fluence used in this work, which showed little triplet generation. Hence, a fraction of geminate recombination of about 50% as reported previously is a good estimate of the upper limit. Apart from fast non-geminate recombination competing with charge extraction, the fill-factors of PCPDTBT:PC60BM blends are also affected by field-dependent charge generation as recently demonstrated by Albrecht et al. Finally we add that in contrast to the TA measurements very recently presented by Tamai et al. our experiments did not unambiguously reveal a difference between polarons in disordered and ordered polymer regions. We found the charge-induced absorption around 100 nm assigned to polarons in disordered regions by Tamai et al. to be rather weak in our samples. A likely explanation is that our PSBTBT polymer had a significantly higher molecular weight of $M_n = 16,000 \text{ g mol}^{-1}$ and $M_w = 60,000 \text{ g mol}^{-1}$ and thus could be much better ordered having mostly semicrystalline regions than the PSBTBT used by Tamai et al., which had a $M_n$ and $M_w$ of only $8,500 \text{ g mol}^{-1}$ and $17,000 \text{ g mol}^{-1}$, respectively, and likely more disordered regions.

Conclusions

The charge generation in the low-bandgap polymer:fullerene blends PCPDTBT:PC60BM and PSBTBT:PC70BM depends on the blend’s nanoscale morphology. In PCPDTBT:PC60BM blends the nanoscale morphology is clearly affected by solvent additives as revealed by 2D solid-state NMR experiments. Enhanced demixing induced by solvent additives turns on diffusion-limited exciton dissociation on a sub-10 ps timescale as larger polymer-rich domains are created. Without solvent additives an intimately mixed blend is obtained and charge transfer after excitation of the polymer is exclusively ultrafast. However, after excitation of the fullerene-rich domains diffusion-limited exciton dissociation is always observed. The exciton dissociation dynamics in PSBTBT:PC70BM blends closely resemble those of the PCPDTBT:PC60BM blend prepared with solvent additives as the demixing of the blend’s components is enhanced by the higher degree of molecular order for the PSBTBT-rich domains even without the use of solvent additives as demonstrated by our solid-state NMR experiments. Apart from the generation of free charge carriers the evolution of another excited state is observed on the sub-nano timescale as confirmed by evolving factor analysis of the NIR TA data. Model-free multivariate curve resolution of the TA data surface shows that the onset of generation of the second component is intensity-dependent and a comparison of the component-associated spectra extracted by MCR-ALS with the spectra of charges and triplets obtained from independent sensitization experiments allows to assign the second component to the polymer’s triplet state likely created by non-geminate recombination of free charges. A comparison of the triplet dynamics of the different polymer-fullerene blends reveals that triplet state generation is suppressed in PSBTBT:PC70BM compared to PCPDTBT:PC60BM prepared with ODT, most likely due to the enhanced crystallinity of the PSBTBT polymer suppressing the encounter of charges at the interface, enhancing the delocalization of interface states, and thereby reducing the non-geminate recombination of free charges in turn leading to the significantly higher device performance for PSBTBT:PC70BM blends compared to PCPDTBT:PC60BM blends.

Acknowledgements

F. Etzold acknowledges financial support from the Max Planck Graduate Center (MPGC) with the Johannes Gutenberg-University Mainz and from the Deutsche Forschungsgemeinschaft (DFG) in the framework of the priority program 1355 (SPP 1355) “Elementary Processes in Organic Photovoltaics” and R. Tilch for help with sample preparation. F. Laquai thanks the Max Planck Society for funding the Max Planck Research Group. I.A. Howard thanks the Alexander von Humboldt Foundation and the Max Planck Society for research scholarships. N. Forler acknowledges a research scholarship of the Max Planck Society. M. R. Hansen acknowledges financial support from the Villum Foundation under the Young Investigator Programme (VVK023122). A. Melnyk thanks the Graduate School Materials Science in Mainz (MAINZ) for support.

Notes and references
