

Improved Film Morphology Reduces Charge Carrier Recombination into the Triplet Excited State in a Small Bandgap Polymer-Fullerene Photovoltaic Cell

By Daniele Di Nuzzo, Aranzazu Aguirre, Munazza Shahid, Veronique S. Gevaerts, Stefan C. J. Meskers,* and René A. J. Janssen*

Photovoltaic energy conversion provides a renewable source of energy that may meet the global energy demand. In particular, polymer photovoltaics are of interest because these may be produced in large surface areas with economic use of raw materials. This prospect has spurred research on polymer solar cells and recently cells with high efficiency and good coverage of the solar spectrum have been demonstrated.^[1–23] The photoactive layer in these polymer solar cells is a bulk heterojunction (BHJ) consisting of a small bandgap polymer acting as electron donor and a low molecular weight fullerene derivative as acceptor. Detailed studies on such a BHJ involving the small bandgap polymer (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] PCPDTBT) illustrates the extreme importance of processing conditions when making these junctions from solution.^[4–8] Here, the use of processing additives was found to boost the power conversion efficiency by a factor of 2.^[4,6] The additives were found to influence the morphology of the blend. In principle, the change in morphology can enhance the performance in several ways. The optimized morphology may allow for faster and therefore more efficient transport of photogenerated free charge carriers. In addition, the efficiency for free charge carrier generation out of the primary photoexcitations may be enhanced in the optimized morphology.

In this study we focus on the efficiency of carrier generation and show that for the non-optimized morphology obtained from processing PCPDTBT polymer without additives, the generation of free charge carriers is reduced because of recombination of the photogenerated hole and electron to a long-lived, low lying electronic state with triplet spin signature.^[9–13] Using processing additives, the formation of these triplet excitations can be suppressed, favoring the formation of free charge carriers out of the charge transfer (CT) state resulting from the photoinduced electron transfer in the BHJ.

In **Figure 1** we illustrate the influence of the processing additive diiodooctane (DIO) on the performance of a solar cell with PCPDTBT:PCBM in a 1:2 weight ratio as active layer. As can be seen, use of the additive during film formation leads to substantial increase in short circuit current J_{sc} and an improvement in fill factor from 0.41 to 0.52. In contrast, the open circuit voltage V_{oc} decreases from 0.69 to 0.62 V.

The charge generation process in the active layers prepared with and without processing agent was studied using near steady state photoinduced absorption (PIA) spectroscopy. This technique provides a sensitive probe for the long-lived excitations in films. In **Figure 2a** we compare the PIA spectra for the two films on quartz substrate. We notice three striking differences between the two PIA spectra. First, after processing with DIO, the PIA intensity at 0.3 eV is much higher. Second, DIO induces an intense PIA band with a maximum at 0.88 eV, while without DIO, a band with a maximum at 0.95 eV is obtained. Third, the magnitude of the bleaching signal relative to the 0.9 eV absorption band is much higher upon processing with DIO. These differences indicate that the long lived excitations in the films with and without processing additive are actually different. As will be detailed below, use of the additive during spin coating leads to long-lived photoinduced charges in the film, whereas without additive neutral photoexcitations on the small bandgap polymer with *triplet* spin character are responsible for the PIA.

To support this assignment we have first studied PCPDTBT mixed with PCBM in toluene solution. For this mixture, we observe an intense PIA band at 1.0 eV, but essentially no signal below 0.5 eV (**Figure 2b**). For only PCPDTBT in toluene solution, we observe the same bandshape, but with a 20 times lower intensity. We assign the 1.0 eV PIA signal to a triplet-triplet absorption originating from the lowest excited triplet state on the polymer ($T_n \leftarrow T_1$). In neat film of PCPDTBT at low temperature we also observe this triplet signal but here the $T_n \leftarrow T_1$ PIA band has shifted slightly to lower photon energies (0.95 eV). We attribute this shift to aggregation effects of the polymer chain and the reduced temperature.

In PIA experiments, this triplet excitation can be distinguished from charge carrier absorption by looking at signals in the 0.3 eV energy range. Chemical oxidation of the polymer to the corresponding radical cation in solution and in solid film shows that the polaronic, positive charges on the PCPDTBT polymer are characterized by *two* absorption bands, one at 0.9 eV and one at ~0.3 eV (**Figure 2c**) that are attributed to the dipole allowed $D_1 \leftarrow D_0$ and $D_2 \leftarrow D_0$ transitions of the

[*] D. Di Nuzzo, Dr. A. Aguirre, Dr. M. Shahid, V. S. Gevaerts, Dr. S. C. J. Meskers, Prof. R. A. J. Janssen
Molecular Materials and Nanosystems
Eindhoven University of Technology
PO Box 513, 5600 MB Eindhoven (The Netherlands)
E-mail: s.c.j.meskers@tue.nl; r.a.j.janssen@tue.nl
D. Di Nuzzo, Dr. M. Shahid, V. S. Gevaerts
Dutch Polymer Institute (DPI)
P.O. Box 902, 5600 AX Eindhoven (The Netherlands)

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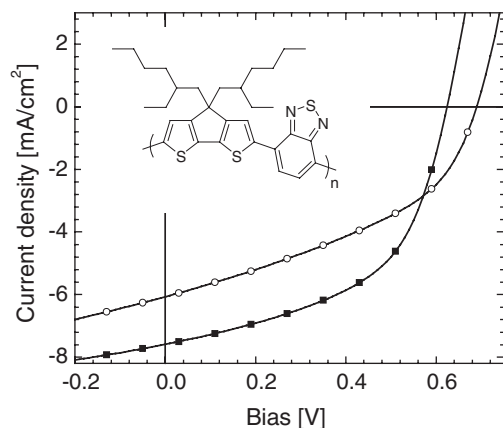


Figure 1. Current density as a function of bias voltage for PCPDTBT:[60]PCBM (1:2 weight ratio) solar cells made by spin coating from chlorobenzene using diiodooctane as processing with additive (solid markers) and without (open markers). The structure of PCPDTBT is shown in the inset.

doublet state radical cation of PCPDTBT. In contrast, the lowest triplet excited state shows only *one* PIA band in the mid infrared. These optical features of the charged and triplet states of PCPDTBT are characteristic for π -conjugated polymers.^[14,15]

An important parameter determining the outcome of photoinduced processes in donor acceptor blends, is the difference between the energy of the lowest triplet excited state, E_T , and that of the charge transfer state, E_{CT} . The energy for the triplet state of PCPDTBT, E_T , is not known exactly, but can be estimated from the following experiments. In the presence of PCBM, the signal for the T_1 state on the polymer in solution is much more intense, while at the same time any $T_n \leftarrow T_1$ absorption from PCBM at 1.73 eV^[16] is absent (Figure 2b). This indicates that the T_1 state on the polymer can be populated by transfer of energy from the T_1 state of PCBM. The latter is formed efficiently via intersystem crossing from the singlet excited state of the fullerene and has an energy of 1.5 eV. Hence E_T of PCPDTBT must be below 1.5 eV. Additional experiments on triplet-triplet energy transfer in solution showed that energy can be transferred from rubrene ($E_T = 1.14$ eV^[17]) to the polymer, while transfer of triplet energy occurs from the polymer to bis(trihexyloxy)silicon-2,3-naphthalocyanine ($E_T = 0.93$ eV^[18]). Furthermore, in solution the T_1 excited state on the polymer is quenched by molecular oxygen through a process that generates 1O_2 ($E = 0.98$ eV). From this we deduce that for PCPDTBT $E_T \approx 1.0$ eV. Empirically, it has been found that E_{CT} is approx. 0.45–0.47 eV higher than $q_e V_{oc}$ in polymer fullerene heterojunctions.^[11,19] and hence we estimate $E_{CT} \approx 1.1$ eV for PCPDTBT:PCBM. This estimate correlates well with the observation of the CT emission in PCPDTBT:PCBM blends which maximizes at ~ 1.20 eV.^[20] From this we conclude that the triplet excited state is equal or lower in energy than the CT state.

We now address the question of how the triplet excitations in the films without additive are formed, see also Figure 3. Measurements of the photoluminescence from the PCPDTBT polymer in solid film, show a dramatic reduction of the intensity of this signal of more than a hundredfold upon inclusion of PCBM in the films. This implies that the lifetime of the singlet excited state from which the luminescence originates,

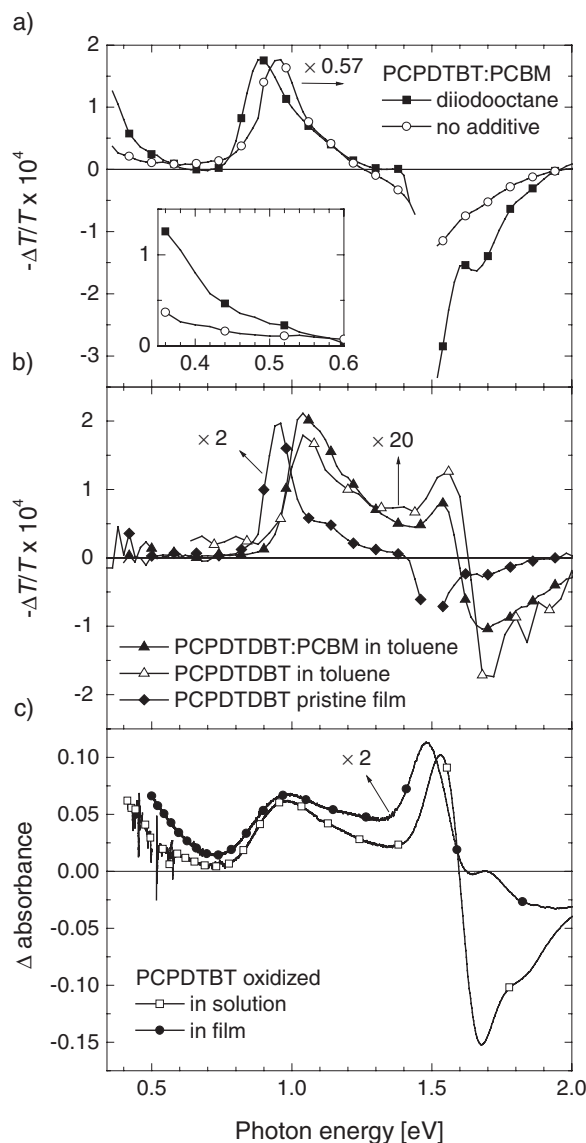


Figure 2. a) PIA spectra of films of PCPDTBT:[60]PCBM (1:2 weight ratio) processed by spin coating from chlorobenzene with (solid squares) and without diiodooctane (open circles). Excitation photon energy $E_{ex} = 1.49$ eV, $T = 80$ K. b) PIA spectra of PCPDTBT:[60]PCBM (1:1) (solid triangles) and PCPDTBT (open triangles) in toluene solution, $E_{ex} = 2.54$ eV, $T = 293$ K. PIA spectrum of a pristine PCPDTBT film (solid diamonds). $E_{ex} = 1.49$ eV, $T = 80$ K. c) Differential absorbance for PCPDTBT induced upon slight oxidation in solution (open squares) with thianthrenium hexafluorophosphate (solid triangles) and in a solid film with chloranil (circles) at $T = 293$ K.

is reduced at least a hundred times. In consequence, also the yield for formation of the T_1 from the S_1 state by direct intersystem crossing must be strongly reduced. Combined with the high intensity of the PIA signal in the mixed film, this indicates that the T_1 excited state in the blend is populated via recombination of geminate charge carriers in the charge transfer state at the donor acceptor interface.^[9–13] In order for this recombination to the T_1 state to be an efficient process, the energy of the CT and charge separated states of the polymer:PCBM

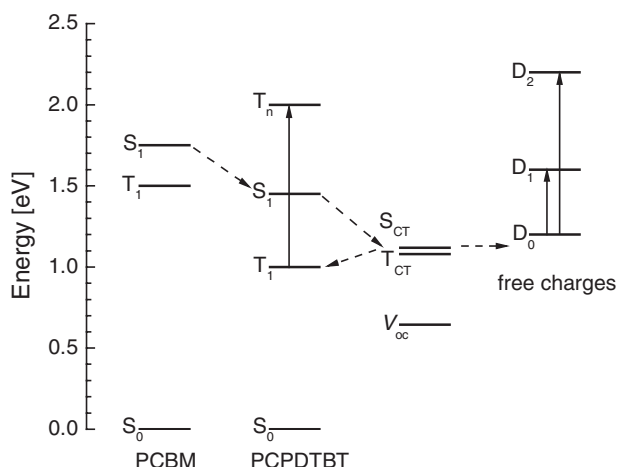


Figure 3. Jablonski diagram illustrating formation of triplet and charge transfer excitations as well as free charges in PCPDTBT:PCBM blends. Important transitions in photoinduced absorption for these excitations are indicated with solid arrows. Dashed arrows represent non-radiative processes.

heterojunction should be positioned above E_T . For efficient population of the triplet state from the CT state the energy difference $E_{CT} - E_T$ should be > 0.1 eV,^[13] consistent with the estimates of the energy levels involved. The recombination to the triplet state from the CT level can be spin allowed, provided that the CT level lives sufficiently long for spin dephasing to occur.^[10] Formation of triplet excitations is also observed in films of PCPBTBT:[70]PCBM. Incidentally, in previous spectroscopic studies on PCPDTBT:PCBM blends, photoinduced absorption near 1 eV was assigned exclusively to photogenerated charge carriers on PCPBTBT.^[21–23] However, it now appears that conclusive evidence on charge carrier dynamics also requires the PIA in the 0.5–0.3 eV range to be probed. This is because both photoinduced charges and triplet photoexcitations contribute to PIA at 1 eV, displaying even a very similar bandshape.

Finally we discuss the influence of the processing additive on the morphology of the films and relate it to photophysics. Previous studies have shown that the additive induces aggregation of polymer chains into more ordered supramolecular polymer structures prior to complete drying.^[5,24] Optical spectroscopy on the $S_1 \leftarrow S_0$ transition of the polymer in our films, fully support this view (Figure 4a). The red shift of the onset of absorption observed, is typical for aggregation of π -conjugated polymers. Additionally, transmission electron microscopy (TEM) (Figure 4b and Figure 4c) shows more pronounced contrast in the mixed film when using DIO. In agreement with earlier reports,^[5,24] TEM shows that the use of DIO induces formation of fullerene clusters that appear dark in the TEM and of polymer fibrils with a diameter on the order of a few nanometer.^[6] These changes indicate phase separation of the two components on a larger length scale into polymer and PCBM domains with higher purity. Such a morphology enhances carrier mobility in each of the subphases. In the Onsager-Braun model for charge generation,^[25] the higher mobility allows geminate charge carriers to escape from their mutual attraction more efficiently. At the same time it allows carriers to reach the lower energy levels in their inhomogeneously broadened density of states, through

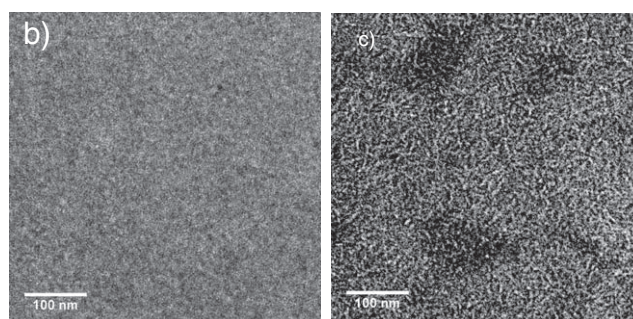
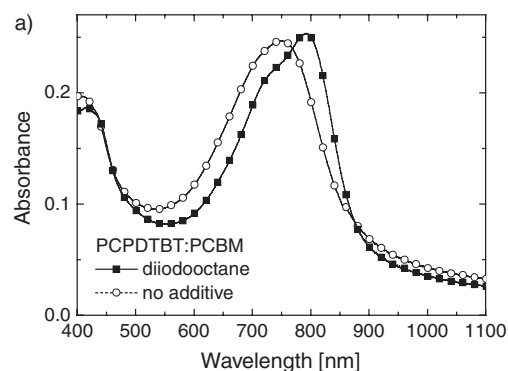


Figure 4. a) Absorption spectra of PCPDTBT:[60]PCBM (1:2 weight ratio) thin films prepared by spin coating from chlorobenzene without (open circles) and with (solid squares) diiodooctane. b) and c) TEM images of PCPDTBT:PCBM films processed without and with diiodooctane. The white bar represents 100 nm.

rapid diffusional motion. This effectively lowers the energy of the charge separated states, allowing the CT state to dissociate more efficiently into free carriers. If the effective energy of charge separated states drops below E_T , recombination into the triplet state is further suppressed. An experimental indication for the lowering of the energy of the charge transfer states upon using additive is the reduction of V_{oc} .

In conclusion, we find that the use of processing additive for deposition of small bandgap polymer:fullerene bulk heterojunctions can raise the yield of photoinduced free carrier formation by suppressing the recombination of photogenerated carrier into the lowest triplet excited state of the polymer. This can, at least partly, explain the enhanced energy conversion efficiency induced by the use of processing additives. The results illustrate that for efficient polymer solar cells, the energy of the lowest triplet state of the polymer must be properly adjusted with respect to the energy of the charge transfer and charge separated states. This may be achievable through control over the morphology.

Experimental Section

Device Preparation and Optoelectronic Characterization: Photovoltaic devices were made by spin-coating poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin-casting in air at 2000 rpm, using a chlorobenzene solution containing 10 mg/mL PCPDTBT ($M_n = 27700$ g mol⁻¹, PDI 1.9), 20 mg/mL [6,6]-phenyl-C₆₁-butyric acid methyl ester [60]PCBM (Solenne) and, optionally,

50 mg/mL of 1,8-diiodooctane (DIO). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at $\sim 3 \times 10^{-7}$ mbar. The active area of the cells was 0.162 cm². *J*-*V* characteristics were measured under ~ 100 mW/cm² white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. The mismatch factor of this lamp to the AM1.5 (100 mW/cm²) spectrum was not determined for the PCPDTBT:PCBM devices.

Thin Film Preparation: Films for PIA were prepared on quartz substrates using the same condition as for solar cell preparation. Film thicknesses were between 60 and 70 nm as measured using profilometry.

Microscopy: Transmission electron microscopy was performed on a Tecnai G² Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref.^[24]).

Spectroscopic Measurements: Near steady-state photoinduced absorption (PIA) spectra were recorded between 0.35 and 2 eV by excitation with a mechanically modulated (275 Hz) laser source and by measuring the change in transmission of a tungsten-halogen probe beam through the sample (ΔT) with a phase sensitive lock-in amplifier after dispersion with a monochromator and detection using Si, InGaAs, and cooled InSb detectors. Pump wavelengths used: 488 nm (2.54 eV, Ar⁺ laser) or 830 nm (1.49 eV, laser diode). The pump power was typically 50 mW with a beam diameter of 2 mm for the argon laser and 130 mW and 1 mm for the diode laser. The PIA signal ($-\Delta T/T$) was corrected for the photoluminescence, which was recorded in a separate experiment. Solutions for PIA were prepared in oxygen free toluene at 300 μ g/mL in an inert atmosphere (H₂O, O₂ < 10 ppm). The measurements were carried out in 1 mm near-IR grade quartz cell at room temperature. The maximal optical density was between 2 and 2.5. Thin films samples were held in an inert nitrogen atmosphere using an Oxford Optistat continuous flow cryostat during PIA measurements. Chemical oxidation of the polymer in *o*-dichlorobenzene solution was induced using thianthrenium hexafluorophosphate^[26] as oxidizing agent. Partial oxidation in solid film was induced by adding 10 wt.% of chloranil.

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