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Low-Temperature Behaviour of Charge Transfer Excitons in Narrow-Bandgap Polymer-Based Bulk Heterojunctions

Dorota Jarzab, Fabrizio Cordella, Jio Gao, Markus Scharber, Hans-Joachim Egelhaaf, and Maria Antonietta Loi*

Photoluminescence studies of the charge transfer exciton emission from a narrow-bandgap polymer-based bulk heterojunction are reported. The quantum yield of this emission is as high as 0.03%. Low temperature measurements reveal that while the dynamics of the singlet exciton is slower at low temperature, the dynamics of the charge transfer exciton emission is temperature independent. This behavior rules out any diffusion process of the charge transfer excitons and energy transfer from these interfacial states toward lower lying states. Photoluminescence measurements performed on the device under bias show a reduction (but not the total suppression) of the charge transfer exciton recombination. Finally, based on the low temperature results the role of the charge transfer excitons and the possible pathways to populate them are identified.

1. Introduction

Bulk heterojunction solar cells have the potential to be among the first ultra-low-cost photovoltaic technologies to come to the market. Due to the solution processability of the organic components, cheap manufacturing techniques such as roll-to-roll or ink-jet printing are possible. With such production methods, it is expected that solar cell modules could reach a watt-peak price considerably below that of inorganic solar cells.[1]

Recently, bulk heterojunction (BHJ) solar cells with efficiencies in the range of 7–8% have been reported and certified by the National Renewable Energy Laboratory (NREL).[2–4] Although the efficiency values are constantly increasing, several different factors limiting the performance of BHJ solar cells have been identified, including imperfect matching of the absorption of the active layer with the solar emission, nanomorphology of the photoactive layer,[5,6] losses due to charge

carrier recombination,[7] inefficient charge transport[8] and the non-optimal offset between the donor and acceptor levels.

The recent development of new polymers with narrow bandgaps represents a great advance in the field, because of the absorption of a larger portion of the solar spectrum. From the first synthesis of 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), a large family of new polymers with bandgaps below 1.4 eV have appeared.[2,9,10]

Blends of PCPDTBT and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) have recently shown interesting device performance.[11,12] Both photophysical[13] and device physics[14] studies on the PCPDTBT:PCBM heterojunction have identified the presence of a bound electron-hole pair (charge transfer exciton), which limits the charge generation yield and causes an electric field dependent recombination loss in solar cells. We recently reported that the charge transfer exciton (CTE) emission in PCPDTBT:PCBM heterojunctions can be suppressed by processing BHJ thin films with octanedithiol (ODT)[15] and in heterojunction containing the homologous polymer poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (Si-PCPDTBT).[13] Recently, Janssen et al. showed that the use of additives in PCPDTBT-based blends suppresses the transfer of the excited population to the triplet state.[16]

In the last few years, a weak optical transition assigned to charge transfer states has been observed in several BHJ.[17–23] Detailed analysis of the ground-state absorption[24] and the photoluminescence of donor-acceptor blends[19,20] and also of the electroluminescence[22] has revealed the presence of an interfacial state of energy lower than the singlet exciton of the polymer. Moreover, it has been observed that the energetic position of the CTE-state correlates with the open-circuit-voltage V_{oc} of BHJ cells,[25] which suggests that the CTE-state is related to the lowest excited state in the system, and that its presence is extremely relevant to the device's function.

In this article we provide a detailed photophysical study of the blend composed by the narrow-bandgap polymer PCPDTBT and PCBM. We confirm some of the features reported for CTE emission in other kinds of BHJ, such as the red-shift with the increasing of the percentage of PCBM in the film[19,23] and the long lifetime of the CTE emission.[19,20] We report for the first time the quantum yield (QY) of the CTE emission, which for

Dr. D. Jarzab, Dr. F. Cordella, J. Gao, Prof. M. A. Loi
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, Groningen, 9747 AG
The Netherlands
E-mail: M.A.Loi@rug.nl
Dr. M. Scharber
Konarka Austria
Altenbergerstrasse 69, A-4040 Linz, Austria
Dr. H.-J. Egelhaaf
Konarka Technologies GmbH
Landgrabenstr. 94, D-90443 Nürnberg, Germany

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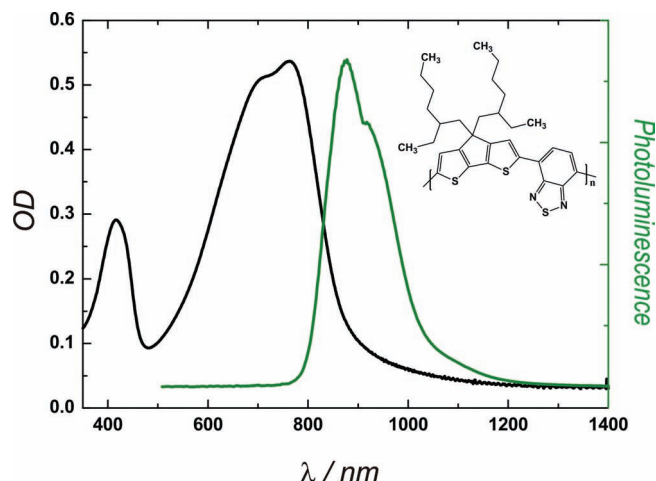www.advenergymat.de

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Figure 1. Absorption and photoluminescence spectra of thin PCPDTBT films. Inset: Chemical structure of PCPDTBT.

PCPDTBT-based blends is as high as 0.03%. Insight in the population mechanism of the CTE in this BHJ is provided by low temperature measurements. From room temperature to 5 K the PL lifetime of the CTE, in contrast to the life-time of the polymeric emission, remains constant. This behaviour rules out any diffusion process of the CTE and energy transfer from this state towards others excited states. Moreover, PL spectra performed in device configuration under bias show a decrease of the CTE emission with no variation of the PL lifetime, indicating that only a small part of the CTE population can be separated by applying a weak electric field.

2. Results and Discussion

Figure 1 shows the absorption and photoluminescence spectra of 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); the chemical structure of the polymer is reported in the inset.

The absorption spectrum of PCPDTBT is broad, with two main peaks at ~415 nm and ~730 nm. The broad absorption band and the narrow band gap (~1.4 eV) make PCPDTBT one of the most promising polymers synthesized in the last year for bulk heterojunction solar cells.

The temperature dependence of the photoluminescence (PL) spectra and decays of a PCPDTBT thin film are reported in **Figure 2**(a) and (b), respectively. The position of the main emission peak at ~872 nm shows no spectral shift with the temperature variation. At low temperature, the spectrum becomes more structured, with the narrowing of the main emission peak and the appearance of a well defined structure at ~978 nm, which is the vibronic peak due to the C = C-backbone vibration at 1250 cm^{-1} of the 0–0-transition at ~872 nm. At T >100 K, the side band results from the superposition of several different vibrations.

The PL decay of PCPDTBT (Figure 2(b)) is mono-exponential with a lifetime of about ~220 ps, which increases with decreasing temperature, reaching a lifetime of ~296 ps at 5 K. The same lifetime is measured in the main emission peak and
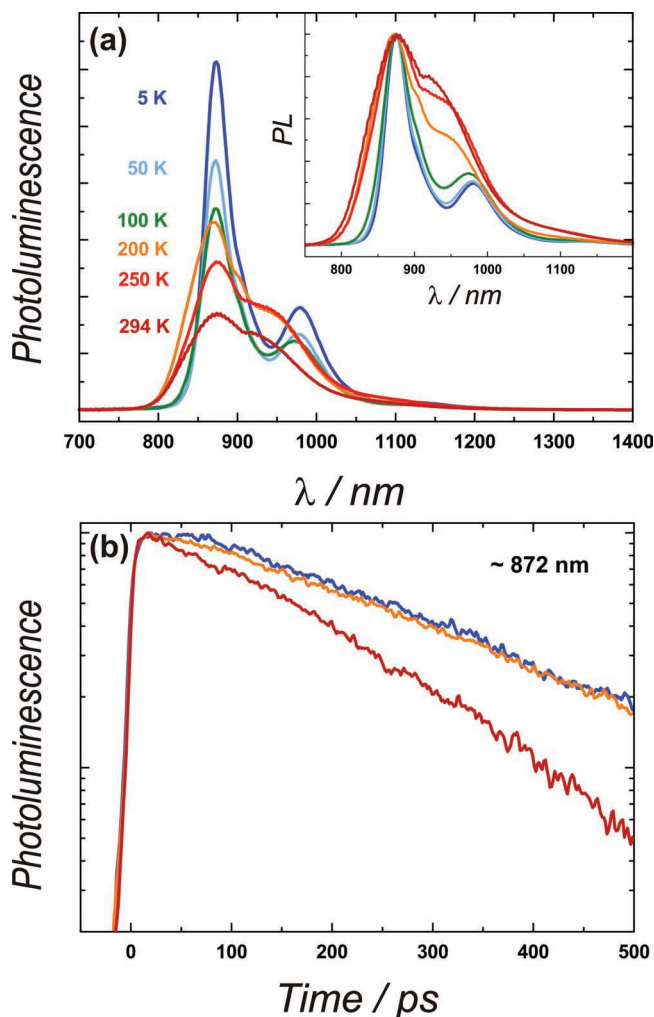

Figure 2. Temperature dependence of a) the photoluminescence spectra of PCPDTBT thin film; b) the PL dynamics at 872 nm. The sample was excited at 380 nm.

in the side peak. It is important to emphasize that the lifetime of PCPDTBT has shown a broad variability, depending on the history of the sample. Freshly prepared samples show longer lifetimes ($\tau \approx 220$ ps) than samples that have been exposed to oxygen also for few seconds ($\tau \approx 78$ ps).

The bulk heterojunction composed of PCPDTBT and PCBM was reported to give rise to solar cells with power conversion efficiency of 3.2%.[26] Using octanedithiol as a processing additive, power conversion efficiencies of up to 5.5% were achieved.[12,15]

The PL spectra of the bulk heterojunction thin films of different ratios of PCPDTBT:PCBM are reported in **Figure 3**. When PCBM is added to the polymer, the PL spectrum shows the appearance of a new feature at low energy that becomes more intense and shifts towards the red with the increase of the amount of PCBM in the blend. This new feature is assigned to the emission of a charge transfer exciton at the interface between the polymer and PCBM phases.[19,20]

For the film with a PCPDTBT:PCBM ratio of 10:1 the PL spectrum already exhibits a tail at low energy that is not present in
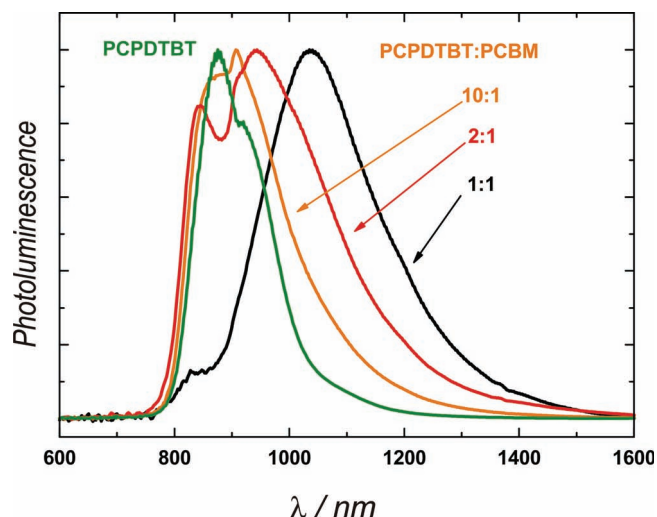
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Figure 3. Normalized photoluminescence spectra of thin films of PCP-DTBT (green line) and PCPDTBT:PCBM heterojunctions of different ratios.

Figure 4. a) False color streak image of the spectrally and time-resolved PL of PCPDTBT:PCBM solar cell (1:1); b) time integrated emission spectra over the initial 30 ps after excitation (blue) and between 50 and 570 ps (red); c) PL dynamics at ~825 nm (red) and ~1075 nm (blue). Green curves in panels (b) and (c) display the emission spectrum and decay, respectively, of the pure PCPDTBT thin film. Excitation wavelength 380 nm.

the pristine polymer. At a composition of the bulk heterojunction of 2 parts of polymer and 1 part of PCBM, the main peak of the polymer is shifted to ~846 nm and a new peak centred at ~944 nm begins to dominate the emission spectrum. When the composition of the film is 1:1, a weak feature is left at shorter wavelengths (846 nm) corresponding to the excitonic peak of the pristine PCP-DTBT, while a new broad emission at ~1037 nm appears.

Both the red-shift of the CTE peak with the increase of the PCBM content and the ratio of intensity between the excitonic and the CTE peak have been previously observed for CTE emission in poly[9,9-(di-n-octyl)fluorene-alt-5,5-(4',7'-di-thienyl-2',1',3'-benzothiadiazole]:PCBM blends.[19,20] The red-shift of the CTE peak is explained as a consequence of the variation of the average dielectric constant of the medium with the increase of the PCBM content[19,20] and has also been observed in electroluminescence measurements.

Here, it is important to emphasize that the CTE is an interfacial state, and that the intensity ratio between the polymer excitonic component and the CTE is subject to variations that depend on the local morphology of the films. Indeed, different intensity ratios of the two peaks have been measured in different sample sets.

Associated with the appearance of the new CTE spectral feature in the emission spectra of the blends, the overall intensity of the photoluminescence emission of the 1:1 BHJ is reduced by about a factor of 100 with respect to the pristine polymer thin film. More quantitative information about the photoluminescence intensity is obtained by measuring the quantum yield (QY) using as reference a near-infrared emitting dye (see experimental section). The QY of the pristine polymer thin film is ~6%, while for the 1:1 PCPDTBT:PCBM BHJ it is ~0.04%. By fitting the emission spectra of the 1:1 BHJ with Gaussian curves, we obtained a contribution of the CTE emission to the total emission intensity of 75%, which results in a QY of the CTE emission of ~0.03%.

As is generally observed in polymer fullerene bulk heterojunctions, the decrease of the singlet excited state emission is
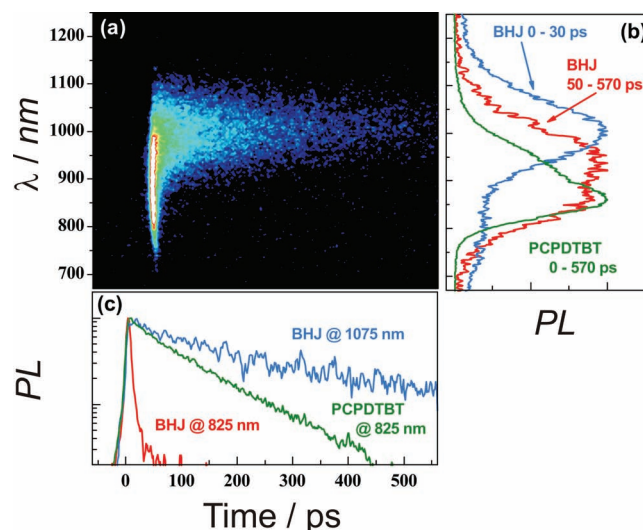
accompanied by the decrease of the PL lifetime. **Figure 4**(a) shows the streak image recorded on the 1:1 blend at room temperature, while panel (b) shows, together with the spectra of the pristine polymer, the spectra extracted from the measurement in (a) in the first 30 ps (blue line) and between 50 ps and 570 ps (red). The PL decay traces of the pristine polymer and of the blend, measured at ~825 nm and ~1075 nm, respectively, are displayed on panel (c). The lifetime of the singlet exciton feature (~825 nm) is ~200 ps in the pristine polymer and <5 ps in the blend, the latter value being limited by the resolution of the setup. The charge transfer exciton emission (~1075 nm) is characterized by a mono-exponential lifetime of ~480 ps. The long lifetime is typical of the charge transfer exciton state. All the different blends studied showed similar lifetimes for the CTE; the only variation observed was related to the presence of a tail of the polymer excitonic emission. In blends of high polymer content, the decay curve at 1075 nm is bi-exponential, due to the superposition of the long-lived mono-exponential CTE emission and the short-lived excitonic emission.

Low temperature PL measurements of the 1:1 PCPDTBT:PCBM blend are reported in **Figure 5**. The evolution of the PL spectra with temperature is shown in Figure 5 (a). The two main peaks assigned to the polymer contribution and to the charge transfer exciton, respectively, show both an intensity increase at low temperature but with a very distinct trend. A better understanding of the variation of the population kinetics of the two emitting states with temperature can be obtained by measuring the photoluminescence dynamics in the two spectral features. Figure 5 (b) shows that the lifetime of the polymer excitonic emission in the BHJ becomes longer at low temperature. The room temperature decay can be fitted with a bi-exponential function, which comprises the short-lived component of ~15 ps and a long-lived one of ~130 ps, at lower
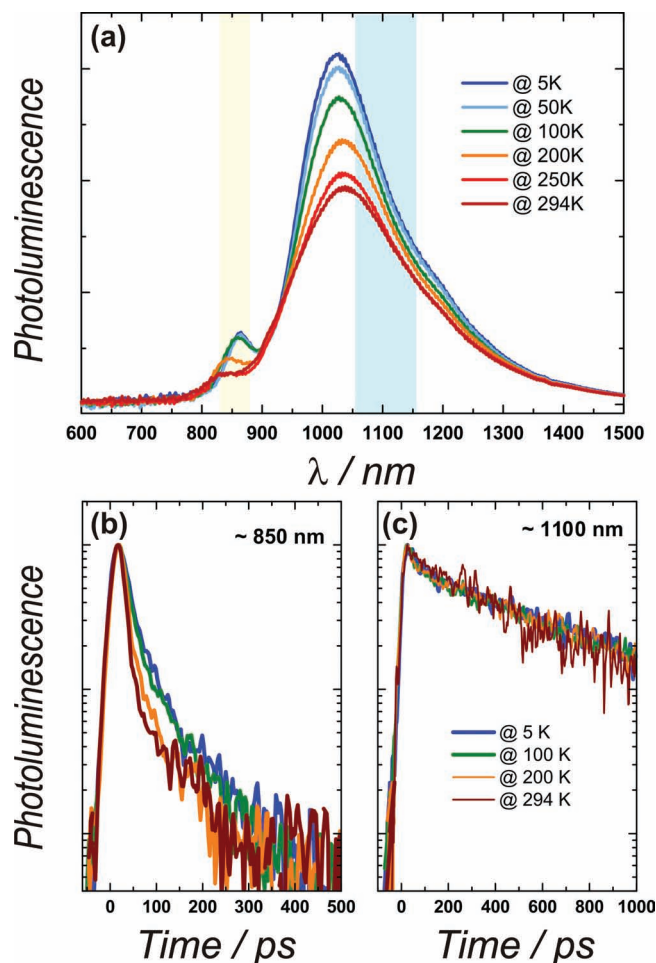
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Figure 5. Temperature dependence of a) PL spectra and b) PL dynamics detected at ~850 nm (the integration area is indicated in the panel (a)) and c) ~1100 nm of thin films of PCPDTBT:PCBM (1:1) (the integration area is indicated in panel (a)).

Figure 6. Photoluminescence spectra of PCPDTBT:PCBM (1:1) solar cell under bias as a function of the applied voltage. Inset: PL dynamics detected at ~1075 nm at different bias.

temperatures the PL decays are also bi-exponential, however they become slower. The trace recorded at 5 K shows the longest decay, characterized by time constants of ~20 ps and ~130 ps; for all temperatures the fast-lived component is dominating, while the long-lived one has a very weak contribution.

The decays of the photoluminescence of the CTE feature at ~1100 nm are reported in Figure 5(c). Interestingly, all the traces recorded at different temperatures appear to be almost perfectly superimposed, with no substantial differences in the fitting of the lifetimes, which can be done with a bi-exponential function with the first time constant equal to 15–20 ps and the second to 480 ps. As discussed previously, the short lifetime appears to be a remaining excitonic emission, while the long component is typical for CTE emission. The CTE lifetime does not change with temperature. However, Figure 5(a) shows an increase of the CTE intensity at low temperature, which, to be in agreement with the measured dynamics, should correspond to an increase of the CTE signal at time t=0. The temperature independence of the CTE dynamics points to the fact that this state is localized and does not participate in diffusion phenomena. Moreover, 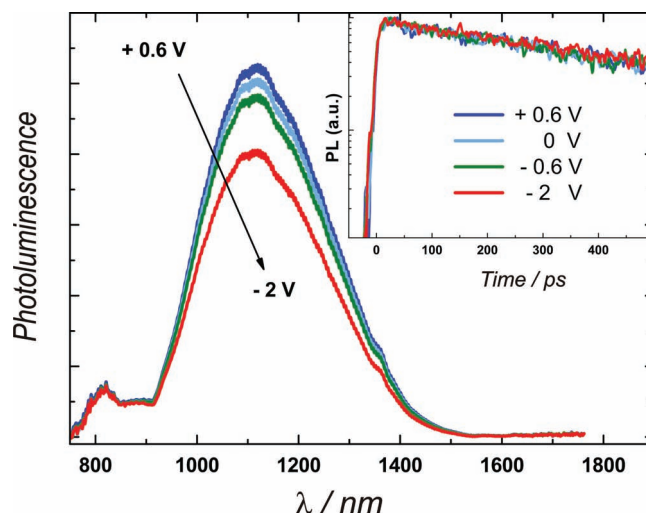no energy transfer from this to other low lying states appears to occur. This finding is extremely relevant for the understanding of the population kinetics of the CTE unravelling the relation with other excited states.

We have investigated the photophysics of CTE in PCPDTBT, obtaining relevant information about population and dynamics. However, their importance in device performances is still under debate.[20,25] To elucidate the role of CTE in the working mechanism of BHJ solar cells, we recorded PL spectra on 1:1 solar cell under different bias conditions. The applied biases are relevant for the device functioning. The spectra are reported without normalization on **Figure 6**. While the remaining polymer emission of the sample does not change with the applied bias, we observed that a small increase of the CTE emission is obtained in forward bias (+0.6V) with respect to the situation at 0V. In reverse bias the PL intensity decreases constantly, reaching ~20% lower signal at −2V. Both the increase in forward bias and the decrease of the intensity in reverse bias have been reported recently for a polyfluorene copolymer.[27] The increase in PL intensity revealed in forward bias can be attributed to the injection of carriers from the electrodes, while the quenching in reverse bias is considered to be a field dependent quenching.[27]

Interestingly, the PL lifes time measured in the same conditions (see inset of Figure 6) are independent of the applied bias. This experimental result together with the PL decrease under bias can be explained by a bias-induced variation of the initial population of the CTE. It is important to note that in the bias range investigated, that is relevant for the operation of the BHJ solar cells, a considerable amount of charges are lost in the radiative recombination of the CTE state.

In **Figure 7**a schematic representation of the excitations in the BHJ is reported. The diagram summarizes all the experimentally evidenced transitions between electronic states. For simplicity the S_0 and S_1 states of the polymer and not the one of the fullerene derivative are depicted. The CTE can be populated both from the ground state[24] and from the polaron pair,[29] the last pathway is evidenced by electroluminescence experiments and by the reported forward bias PL measurements
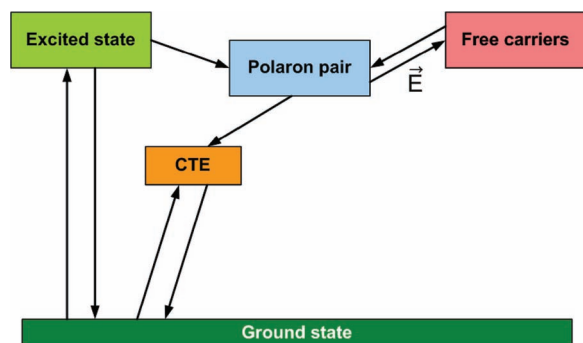
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Figure 7. Schematic representation of the excitation in the BHJ under study. For simplicity only the excited state of the polymer is indicated, triplet levels are also omitted.

(see Figure 6). It is important to note that it is not possible to form polaron pairs from the CTE, this is an obvious result of the temperature independence of the CTE emission and from the dynamics of the PL under bias. The decrease of the CTE population in reverse bias as mentioned before is attributed to a decrease of the population of the state at t = 0. Although it cannot be excluded that a certain fraction of the CTE states is depopulated at times shorter than our experimental resolution.

3. Conclusions

A weak charge transfer exciton emission has been reported in several bulk heterojunctions for organic solar cells. Here we report the CTE emission for a narrow-band-gap based BHJ as efficient as 0.03%.

Low temperature measurements reveal that while the dynamics of the singlet exciton and the electron transfer is temperature dependent, the dynamics of the CTE is temperature independent. This behaviour rules out any diffusion process of the CTE and energy transfer initiating there and allow to drawn a schematic representation of the excitation in the system evidencing that the CTE acts as an interfacial defect of the system.

Measurements performed under bias confirm the reduction but not the suppression of the CTE population also at limited bias, and the unchanged dynamics point to the reduced formation of the interfacial state under bias.

4. Experimental Section

Spectroscopy: Photoluminescence measurements were performed on thin films blade-coated on cleaned quartz substrates. Samples were excited by a 150 fs pulsed Kerr mode locked Ti-sapphire laser at 760 nm or frequency doubled at 380 nm. The steady state photoluminescence emission was measured with an Andor iDus InGaAs array detector. The spectra were corrected for the spectral response of the set up. Typical excitation power densities were ~1 mW on a focused laser spot of about 100 μm of diameter. Time-resolved PL was recorded by a Hamamatsu streak camera working in synchro-scan mode. All measurements were performed on samples edge-sealed with a glass slide and an UV-curable epoxy in a N_2-filled glovebox. To avoid any exposure to oxygen, low temperature measurements were also performed on encapsulated samples loaded in a He-flux Oxford Optistat cryostat. Quantum yield (QY) measurements were performed using as standard the dye LDS

821[28] emitting at ~785 nm and showing a QY of 10% when dissolved in chloroform. The mismatch between the emission spectra of the sample and of LDS 821 was corrected with the response curve of the experimental apparatus.

Sample Fabrication: BHJ devices were prepared as described earlier[26] and encapsulated in inert atmosphere. Chlorobenzene was used as processing solvent.

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