Research Article

Radiative Recombination in Bulk-Heterojunction Solar Cells

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Abstract: We have studied the time-dependent charge transfer emission in a photovoltaic device made of a blend of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclo-penta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3 benzothiadiazole)] and [6,6]-phenyl C_{61}-butyric acid methyl ester, a system showing a low band-gap suitable as absorber for bulk-heterojunction solar cells. We find a short-lived component (~1 ns) and no evidence of a long-lived emission (μs) expected if photo-generated free charge carriers would recombine radiatively via the charge transfer state. Our results explain, why the open circuit voltage loss in the investigated solar cell is much larger compared to GaAs-based or perovskite solar cells and highlight one of the key processes limiting the performance of bulk-heterojunction solar cells.

Keywords: Organic solar cells · charge transfer state · radiative recombination

Introduction

Organic photovoltaics (OPV) have attracted academic and industrial interest, due to their potential as a low cost photovoltaic technology. Besides costs, their short energy pay-back time, the possibility to manufacture flexible and low weight modules and the ability to use semi-transparent organic solar cells for façade integration have been discussed as main advantages of OPV. Enormous progress has been made in the past three decades. Recently, power conversion efficiencies as large as 18.1% could be achieved.[1] Despite all the efforts in advancing this technology, the theoretical upper limit of the power conversion efficiency of organic solar cells is still under debate. In the Shockley-Queisser model,[2] a solar cell is assumed to exhibit only radiative recombination of free charge carriers. In combination with ideal light management, this would lead to an open circuit voltage $V_{oc} = E_g(1 - T_D/T_S)$ where E_g is the band-gap of the absorber, T_D and T_S are the temperature of the device and the sun respectively.[3]

In organic solar cells, the recombination of free charge carriers proceeds via the formation of a charge transfer state (CT) – often also called charge transfer exciton. It is formed between donor and acceptor moieties in the bulk-heterojunction absorber and has become the central topic in discussions of OPV efficiency.[4–7] Based on Rau's reciprocity theorem[8] relating the photovoltaic quantum efficiency and electroluminescent emission of solar cells to each other, Vandewal et al.[4,6] studied the electro-optic properties of several different bulk-heterojunction solar cells. They found a relation between the open circuit voltage of OPVs and the spectral position of the charge transfer state absorbance, photoluminescence and electroluminescence. Due to the excellent agreement between the Rau's reciprocity theorem and their experimental results, the authors concluded that the charge transfer state is *the* emissive species, which needs to be considered for the ultimate efficiency limit in the framework of the detailed balance approach. Based on these findings Gruber et al.,[9] Koster et al.[10] and Vandewal et al.[6] calculated the ultimate

power conversion efficiencies of organic solar cells. They found maximum efficiencies in the range of 20–30% depending on the energetic position and the strength of the CT-absorption, showing that OPVs can be as efficient as their inorganic counterparts, provided that the recombination of photo-induced charge carriers via the CT state is predominantly radiative. Therefore, enhancing the CT-emission and optimizing its energetic position is a promising approach to improve the power conversion efficiency of OPVs. On the other hand, there is some experimental evidence that a strong charge transfer emission is not beneficial for the power conversion efficiency of organic solar cells.[11] E.g. in the low band gap absorber blend PCPDTBT:PCBM (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclo-penta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3 benzothiadiazole)]:[6,6]-phenyl C61-butyric acid methyl ester) a strong charge transfer state emission is found in poorly performing devices. When using a processing additive for device manufacturing, the charge transfer emission is suppressed, while the power efficiency is almost doubled. This is opposite to what is expected considering the detailed balance approach. To shed some light on the observed discrepancy, we have performed a set of time-resolved photoluminescence experiments probing the CT emission in a

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PCPDTBT : PCBM solar cell. Based on a simple model we show that a delayed emission on a µs time scale resulting from the recombination of free charge carriers should be present in the studied system. To be able to observe the dynamics of the weakly emitting CT states in the near-infrared (NIR) spectral region, a Superconducting Single Photon Detector (SSPD) capable to detect single NIR photons with efficiencies about 12% and a time jitter of only a few tens of picoseconds was used for PL decay experiments in the nano- to millisecond range. The experiments do not give any evidence of a delayed emission. This suggests that the recombination of free charges through an emissive charge transfer state is of minimal importance in the studied absorber blend, for which the CT-emission thus functions solely as a loss mechanism prior to the generation of free carriers, and is not a good indicator for high power conversion efficiency of OPVs.

The Model

As discussed in detail by Markvart and Landsberg,[12] the simplest way to describe a solar cell is applying a two-level quantum energy converter scheme (Figure 1). It includes all important processes occurring in a photovoltaic device and leads to the Shockley Queisser Limit when ideal charge transport, photon absorption and radiative recombination of free charges are assumed. Vandewal et al.[6] applied a similar model for the calculation of the thermodynamic losses in the open circuit voltage of a bulk heterojunction organic solar cell. In doing so, the two species are assumed to be the CT-state and free charges in the donor and acceptor moieties (Figure 1a)). The generation rate (G) leads to the population of the CT-state from excitonic donors or acceptors, and all free carrier recombination is assumed to proceed via the CT-state.

The 2-level quantum converter can be characterized using a set of rate equations. Assuming that charge carriers are generated via the charge transfer state and that no charge carriers can leave the absorber volume (at open circuit conditions) the system can be described by equation 1 and 2. G is the generation rate of charge transfer states N_{CT}. k_r is the rate constant for recombination of N_{CT} to the ground state.

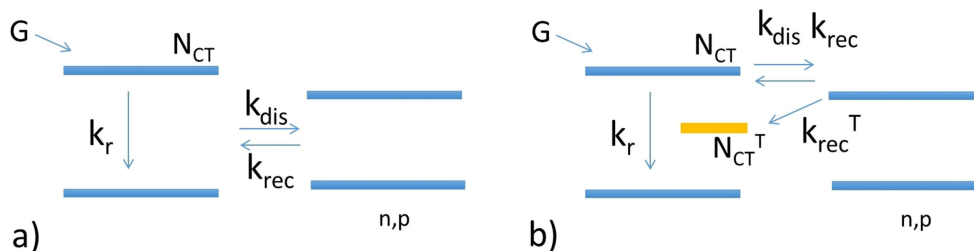$$\frac{dN_{CT}}{dt} = G - k_r \cdot N_{CT} - k_{dis} \cdot N_{CT} + k_{rec} \cdot n^2$$

$$\frac{dn}{dt} = k_{dis} \cdot N_{CT} - k_{rec} \cdot n^2$$

k_{dis} is the rate constants for dissociation of N_{CT} to free charges. k_{rec} is the rate constant for the bimolecular recombination of free charges to the CT state. The steady state solution to Eq. 1 and 2 is used in the detailed balance analysis, but the system must also be consistent with the time resolved luminescence of the CT-state. We were interested in the time-dependent decay of the model system after pulsed excitation, and solved the differential equations numerically assuming G(t) to be a 2 ns square pulse. The rate constants were extracted from available literature data and earlier measurements. The recombination rate constant k_r of the charge transfer state can be extracted from time resolved photo-luminescence measurements reported earlier.[13] A temperature independent emission decay with a lifetime of approximately 1 ns was found resulting in $k_r = 10^9 \, s^{-1}$. The dissociation of charge transfer states into free charges is a very efficient process and occurs on the sub-picosecond time scale, and can be measured by the appearance of polaron signal in photo-induced absorption.[14] We set $k_{dis} = 10^{12} \, s^{-1}$. The recombination of charges can be studied applying transient photo-voltage spectroscopy.[15] For PCPDTBT : PCBM devices charge carrier lifetimes in the µs-regime have been reported. This leads to a bimolecular recombination coefficient $k_{rec} \sim 10^{-10} \, cm^3 \, s^{-1}$.[16] These values are typical for most OPV material systems.

Experimental

Solar cells and thin absorber films were prepared following the procedures reported earlier.[17] Chlorobenzene was used as processing solvent and we investigated conjugated polymer: fullerene blends with weight ratios of 1 : 1. In solar cells, the absorber layer was sandwiched between an poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (AI4083) coated indium-tin-oxide and an aluminium contact. Solar cells with an active area of ~0.25 cm² were tested on a LOT-QD solar simulator (LS0821). The radiation intensity was adjusted using a reference silicon diode to 100 mW cm⁻². External quantum efficiencies (EQEs) were recorded with a home-built setup using a xenon-lamp attached to a monochromator as illumination source, a Jaissle 1002 potentiostat functioning as a

Figure 1. a) 2-level quantum converter, and sketch of decay channels for the charge transfer state and free charge carrier concentrations, b) 2-level quantum converter with an additional lower lying state.

preamplifier and a lock-in amplifier (SR830, Stanford Research Systems) for photocurrent detection. To study the time-dependence of the CT-emission at longer timescales we use a Superconducting Single Photon Detector (SSPD, Scontel Superconducting Nanotechnology) together with a Time-Correlated Single Photon Counting (TCSPC) system (Pico-Harp 300 by PicoQuant). The SSPD shows approximately 12% quantum efficiency in the near IR at $\lambda = 1.31$ μm wavelength and allows time dependent measurements in the nanosecond to the millisecond range. The SSPD consists of a thin superconducting NbN film which is patterned in a compact meander geometry forming a nanowire structure. The detector is cooled below its superconducting critical temperature and biased with a dc current that is slightly below the critical current of the wire. A photon incident on the wire structure results in the formation of a hotspot of excited electrons and, thus, of a transient resistive domain the voltage drop across which can be easily detected as microwave pulse in the readout circuit. The time resolution of the SSPD-system is about 100 ps. Solar cells were excited by a pulsed diode layer (657 nm) delivering ~2 ns pulses (full width half maximum) at repetitions rates between 500 kHz to 2 MHz with a pulse energy of approximately 15 pJ. A microscope objective was used to focus the laser into a spot with 10 μm diameter on the solar cell surface. The sample emission was collected using the same microscope objective and the photons were guided through a single mode fiber to the SSPD. In some cases we applied a second laser (637 nm) to provide additional cw-excitation of the solar cell, or operated the solar cells under different external bias voltages. A 1 mm thick silicon wafer was used as a long pass filter for selecting the low energy part of the emission spectrum originating from the charge transfer emission. A schematic drawing of the experimental setup is shown in the supporting information. Spectrally resolved emission spectra were recorded using an Acton monochromator equipped with a one dimensional InGaAs diode detector array (Princeton Instruments) or a Shamrock 303i monochromator equipped with an iDus420 CCD and an iDus490A detector array (both ANDOR). The optical absorbance was measured with a Perkin Elmer Lambda 1050 spectrometer. All calculation were performed using the software package Mathematica (Wolfram).

Results and Discussions

Figure 2a) shows the chemical structure of the donor polymer PCPDTBT and the acceptor molecule PCBM used in the experiments. Figure 2b) shows the absorbance and the photoluminescence of a thin PCPDTBT film and the photo-
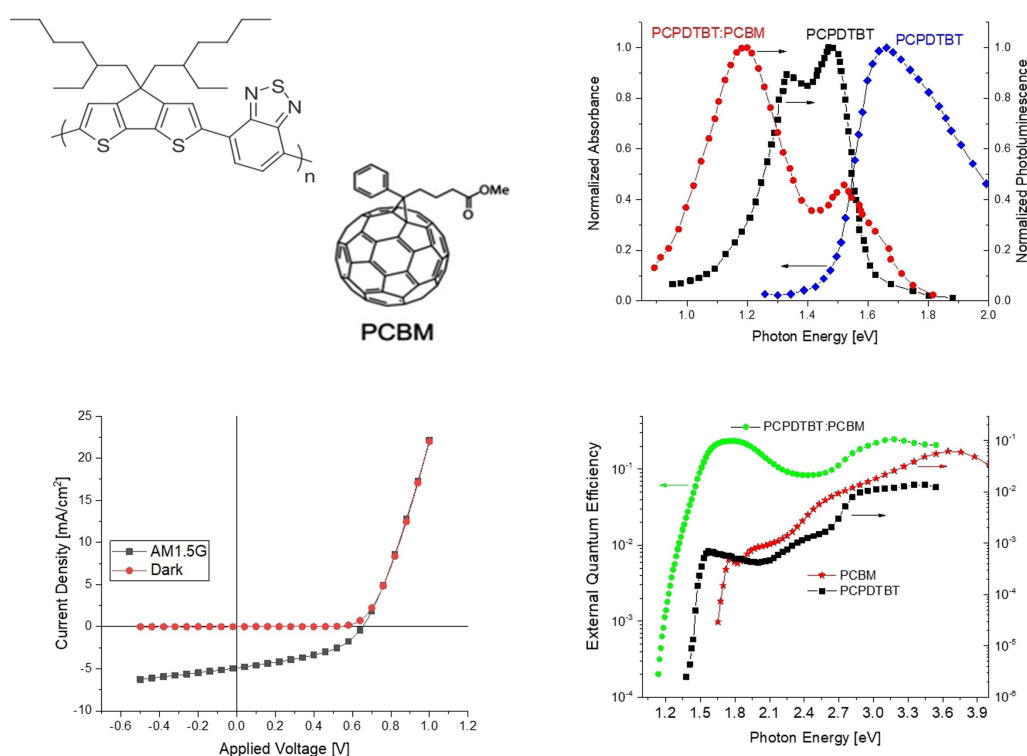

Figure 2. a) Chemical structures of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclo-penta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3 benzothiadiazole)] (PCPDTBT)and [6,6]-phenyl C61-butyric acid methyl ester (PCBM), b) Absorbance and photoluminescence of thin film of PCPDTBT and the photoluminescence of PCPDTBT : PCBM blend (1 : 1 wt %), c) Current-voltage curves of a PCPDTBT : PCBM blend (1 : 1 wt %) based solar cell, d) external quantum efficiency spectra of photodiodes with PCPDTBT, PCBM and PCPDTBTv : PCBM blend (1 : 1 wt %) absorbers.

luminescence of a PCPDTBT:PCBM film (1:1 wt%). All spectra are normalized. The addition of electron acceptor PCBM leads to a strong quenching of the donor polymer emission. In the photoluminescence spectrum of the donor-acceptor blend the emission of the charge transfer state is clearly visible at low photon energies.

Figure 2c) shows the current-voltage curves of the investigated device measured in the dark and under illumination (simulated AM1.5G). In Figure 2d) the external quantum efficiency spectra of the studied PCPDTBT:PCBM solar cell and photodiodes with pristine PCPDTBT and PCBM absorber layers are compared. The onset of the EQE spectrum of the PCPDTBT:PCBM solar cell is significantly shifted to lower energies compared to the EQE of the PCPDTBT-photodiode due to the additional absorption of the charge transfer state present in the donor-acceptor blend.

Equation 1 and 2 were solved numerically with the parameters $k_r = 10^9\ s^{-1}$, $k_{dis} = 10^{12}\ s^{-1}$, $k_{rec} = 10^{-10}\ cm^3 s^{-1}$. A simulated decay curve of the charge transfer state concentration is shown in Figure 3. In addition to a fast decay

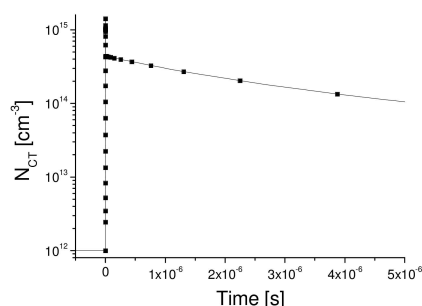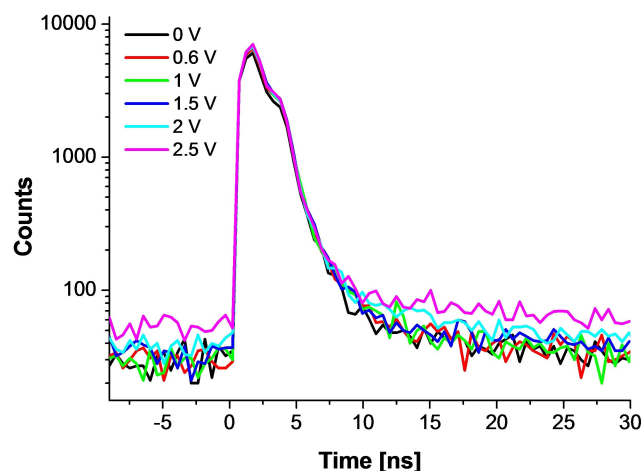component, a long-lived decay with an amplitude of at least a few percent of the short-lived component is present. Assuming a finite probability for radiative recombination, a slow decay component should also be present in the CT-emission. The terms geminate and non-geminate recombination are frequently used to describe the recombination of CT-states that have not yet separated into free charges, and the recombination of free charges via the CT-state respectively. According to these definitions, geminate recombination would correspond to the short-lived component. As these carriers cannot contribute to photocurrent, this is a pure loss mechanism in the solar cell and non-geminate recombination would correspond to the long-lived component.

Our simulation work suggests that over a wide range of parameters, a delayed component of the charge transfer state recombination should be visible in the transient photoluminescence decay. In other words, a simple test for the validity of the proposed model is the investigation of the time-dependence of the CT emission. In Figure 4, emission transients recorded on PCPDTBT:PCBM bulk-heterojunction solar cells operated at different bias voltages are shown. The shape of the decay curve is dominated by the shape of the laser pulse and for all applied voltages only a short lived component is observed.

Operating the device under forward bias leads to electroluminescence and, thus, to a shift of the baseline to higher values. In Figure 4b) a measured transient and a baseline recorded with no photo-excitation are compared. Only a short-lived transient, indicating the radiative decay of photo-excited charge transfer states, is visible. Several different conditions, including variations in the energy of the laser pulse, applying an additional cw-light-bias or operating the device at different external biases were tested. We found small variations in the overall signal intensity but no significant changes in the decay characteristics of the photo-excited species. This is in excellent
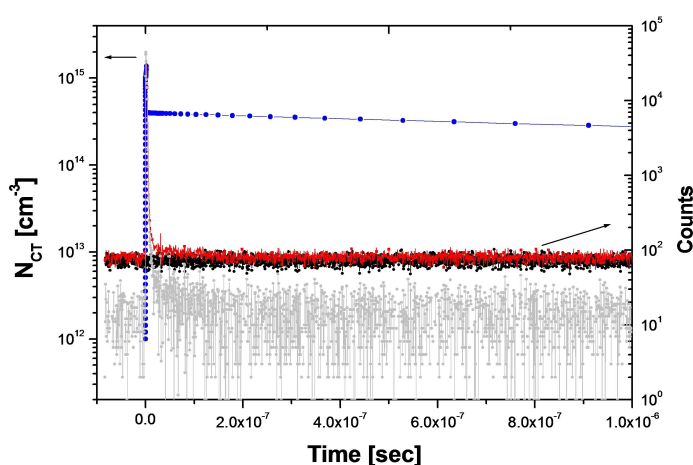

Figure 3. Simulated decay of the photoexcited charge transfer state concentration, cw-Excitation ~3 mW/cm² (637 nm), pulse energy 25 pJ (657 nm), pulse length 2 ns, $k_r = 10^9\ s^{-1}$, $k_{dis} = 10^{12}\ s^{-1}$, $k_{rec} = 10^{-10}\ cm^3 s^{-1}$.

Figure 4. a) Emission transients recorded on a PCPDTBT:PCBM (1:1 wt%) based solar cell with different bias-voltages applied; excitation at 657 nm, 20 pJ per pulse, b) Comparison of a photoinduced transient emission (red) and the baseline (dark counts) recorded under identical experimental conditions (black), the recorded signal with a baseline correction (grey) and the calculated transient.

agreement with earlier measurements on the sub-ns timescale which showed a basically temperature and electrical-bias independent decay of the charge transfer emission.[18] Our findings indicate that the simple quantum converter in Figure 1 does not describe the investigated polymer-fullerene solar cell properly. The complete absence of a long-lived emission suggests that a recombination of free charges through same the charge transfer state involved in the charge generation process is not the dominating process and alternative recombination paths for free charges do exist. The scheme for the photo-excitation and recombination of charge transfer excitons and free charges may be summarized as follows: After photon absorption, excited charge transfer states are generated. A substantial fraction of these states dissociate on a picosecond time scale and they do not contribute to the charge transfer emission. The remaining excited CT-states recombine on the ns time scale and cause the observed CT-emission. Generated free charges predominately recombine to the ground state by non-radiative recombination on a microsecond time scale. This recombination process is facilitated by an additional low energy state present in the donor-acceptor blend (Figure 1b)). The charge transfer state can exist in four different spin-configurations. Due to the fast time-scale, the initially generated CT-state has singlet character. The recombination channel for free charge carriers is predominately the CT triplet state (N_{CT}^T) due to the favourable energetics and spin-multi-plicity. The recombination of the N_{CT}^T may lead to the formation of molecular triplets or a direct deactivation to the ground state. The role of triplet states in donor-acceptor based solar cells has been discussed earlier.[19,20,21] In time-resolved EPR and transient optical studies the enhanced formation of triplet states was observed in blends of PCPDTBT and different fullerene acceptors.[22,23]

The probability for free charges to re-populate the excited CT state (N_{CT}) is very small due to unfavourable energetics and therefore the delayed emission is not detectable in our experiments. The observed CT-emission in the ns-range is a product of purely geminate recombination, and therefore it is a loss mechanism. Our findings explain the observation that CT-emission does necessarily correlate with high PCE of state-of-the-art bulk heterojunction solar cells. In contrast to the frequently applied charge-transfer-state analysis[4,6], our experimental results also suggest that a strong CT-emission observed in photoluminescence experiments on donor-acceptor blends is not necessarily a good selection criterion for high performance materials.

Summary

We have investigated the time-dependent emission of the charge transfer state in bulk-heterojunction solar cells based on a PCPDBT:PCBM absorber layer. Assuming that photo-induced free charge carriers recombine via the charge transfer state, a delayed CT-emission is expected. In our experiment, we do not observe a delayed component in the CT photo-luminescence. This suggests that the majority of CT-emission does not originate from the recombination of long-lived photoinduced charges. The observed CT-emission occurs prior to free charge generation leading to a loss of charges carriers. This explains earlier findings that a strong CT-emission does not necessarily lead to higher power conversion efficiencies.

In searching for the theoretical and practical upper limit for OPV efficiency, a radiative recombination mechanism of free charges with a lifetime in the range of μs or longer will be required in bulk-heterojunction absorber layers. Increasing the energy of the CT-state by optimising the energy levels of the donor and acceptor molecule could be one promising approach to foster radiative recombination of free charges.

Acknowledgements

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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