

# Femtosecond up-conversion technique for probing the charge transfer in a P3HT : PCBM blend via photoluminescence quenching

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## Abstract

We report on an experimental study of the charge transfer dynamics in a P3HT : PCBM blend by means of a femtosecond fluorescence up-conversion technique. Using two-photon excitation we probe the exciton dynamics in P3HT and a P3HT : PCBM blend with a weight ratio of 1 : 1 at excitation densities of up to  $6 \times 10^{18} \text{ cm}^{-3}$ . In both samples we find strongly nonexponential decay traces compatible with (i) diffusion-limited exciton–exciton annihilation and (ii) diffusion-limited donor–acceptor charge transfer in the polymer blend. Additionally, our results indicate that in the P3HT : PCBM blend about 50% of the photogenerated excitons undergo a prompt charge transfer process on a time scale of about 150 fs. Our study shows that fluorescence spectroscopy with femtosecond time resolution is a powerful technique for probing ultrafast charge transfer processes in solar cell materials.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Conjugated polymers are the subject of intense research efforts in the field of materials science and have attracted an ever-increasing interest in the last years due to their promising optoelectronic applications in, for example, solar cells, light-emitting diodes and displays. Therefore, numerous experimental as well as theoretical studies focus on the photophysical properties of these substances and on their exploitation for the further development of optoelectronic devices (for recent reviews see [1, 2]). In organic bulk-heterojunction solar cells, conjugated polymers are utilized as light absorbing and electron donor moieties, while a second species is added as an electron acceptor. An efficient and ultrafast charge separation at the donor–acceptor interface is crucial for overcoming the short diffusion lengths for excitations in the polymer ( $\sim 10 \text{ nm}$ ) which result from comparatively low carrier mobilities and

short exciton lifetimes ( $\sim 100 \text{ ps} - 1 \text{ ns}$ ). Blends of the poly(3-hexylthiophene) (P3HT) and the methanofullerene C<sub>61</sub>-butyric acid methylester (PCBM) have been shown to give rise to sub-picosecond charge transfer dynamics [3, 4], and power conversion efficiencies in P3HT : PCBM based devices up to 5.1% have been obtained with relative weight ratios in the region of 1 : 1 [5, 6].

From photoinduced absorption and pump–probe spectroscopic studies on blends of poly(paraphenylene-vinylene) (PPV) derivatives and fullerenes, ultrafast charge carrier generation within less than 100 fs has been found to take place upon photoexcitation [3, 7]. For P3HT : PCBM composites, similar measurements limited in time resolution to 200 ps, pointed also to ultrafast charge transfer dynamics [8]. So far, all of these time-resolved studies have been using nonlinear absorption techniques. In addition, it is highly desirable to probe the charge transfer dynamics in solar cell devices by means of time-resolved fluorescence techniques, for example, femtosecond

fluorescence up-conversion, since such fluorescence measurements (i) give direct access to the exciton relaxation and recombination dynamics, (ii) can provide higher sensitivity than nonlinear absorption techniques and (iii) can easily be combined with high resolution microscopy techniques potentially providing access to combined time- and space-resolved studies of the carrier dynamics in organic semiconductors.

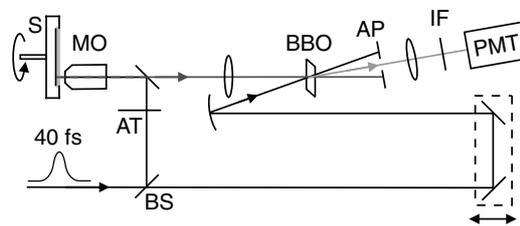
However, little research work has been reported up to now along this direction. The femtosecond up-conversion technique was successfully used in photoluminescence (PL) quenching experiments on PPV-wrapped carbon nanotubes [9] and on thin solid films of poly(phenyl-*p*-phenylene-vinylene) (PPPV) blended with polycarbonate [10]. The results of these studies emphasize the feasibility of ultrafast PL measurements to shed light on the dynamics of the creation and decay of excitons upon photoexcitation which remain in the focus of current research [11, 12].

In this paper, we report on first sub-picosecond time-resolved PL quenching measurements on pristine P3HT samples and polymer : fullerene blends with a 1 : 1 weight ratio using a fluorescence up-conversion technique with two-photon excitation. In both samples we find strongly nonexponential decay traces revealing diffusion-limited exciton–exciton annihilation as well as diffusion-limited donor–acceptor charge transfer in the polymer blend. Additionally, our results indicate that in the P3HT : PCBM blend about 50% of the photogenerated excitons undergo a rapid, nondiffusive charge transfer process on a time scale of about 150 fs. Our study shows that time-resolved fluorescence spectroscopy is a powerful means of probing the carrier dynamics in solar cell materials on ultrafast time scales.

## 2. Experimental

The sample preparation as well as all measurements were performed in a nitrogen atmosphere to avoid possible influences of oxygen diffusion into the sample on the experimental results. Regioregular P3HT (Sigma-Aldrich) and PCBM (Nano-C) were both used as purchased without further purification. Equal amounts were dissolved in chloroform at  $10.8 \text{ mg ml}^{-1}$  and  $10.3 \text{ mg ml}^{-1}$ , respectively, and then mixed in order to produce blends of about 1 : 1 in weight. For steady-state spectroscopic measurements, thin films with a thickness of about 200 nm were produced by spin-coating  $80 \mu\text{l}$  of solution or solution mixture onto fused silica substrates. For the femtosecond up-conversion measurements a considerably larger film thickness was required to enhance the signal-to-noise ratio. Therefore,  $40 \mu\text{l}$  of solution were drop-cast onto the substrate, yielding a spatially homogeneous layer of  $\sim 5 \text{ mm}$  in diameter and an average thickness of roughly  $200 \mu\text{m}$ . To maintain a nitrogen atmosphere during the measurements, the samples were mounted into a sealed cell with thin glass windows.

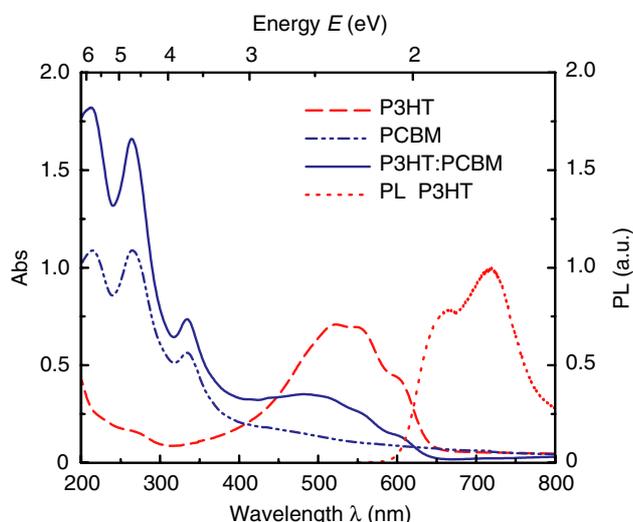
For recording steady-state PL spectra of P3HT, 15 ps laser pulses at a wavelength of 327 nm and a repetition rate of 4 MHz were focused onto the sample to a spot size of about  $100 \mu\text{m}$ . The pulses with an energy of  $\sim 100 \text{ pJ}$  were generated by a synchronously pumped, cavity-dumped



**Figure 1.** Schematic of the PL up-conversion setup. 40 fs pulses from a Ti : sapphire oscillator operating at 800 nm are focused at a pulse energy of 1 nJ through a microscope objective (MO) to a  $3 \mu\text{m}$  spot size onto the rotating sample mounted into a sealed cell with glass windows maintaining a nitrogen atmosphere (S). The two-photon-induced photoluminescence is collected and time-gated in a BBO crystal. The up-converted signal is detected using a cooled PMT.

DCM dye laser system and second-harmonic generation in a  $\text{LiNbO}_3$  crystal. The sample PL was collected in reflection, dispersed in a 0.5 m monochromator and detected by a liquid-nitrogen-cooled back-illuminated charge-coupled device (CCD).

For time-resolved PL measurements, a femtosecond up-conversion setup (figure 1) was used, which is similar to the one described previously [13]. A Ti : sapphire laser system produced 40 fs pulses at a centre wavelength of  $\lambda_L = 800 \text{ nm}$  and a repetition rate of 80 MHz. The excitation pulses with energies of about 1 nJ were focused to a spot size of about  $3 \mu\text{m}$  onto the sample using a 0.35 NA MO. To avoid excitation-induced bleaching effects, the sample cell was mounted on a rotation stage (S), rotating at about 20 Hz and the focal spot was off-set by 2 mm from the rotation axis. The PL induced by two-photon absorption was collected from the sample cell via the same MO, focused into a 3 mm thick beta-barium-borate (BBO) crystal and mixed with the time-delayed gate pulses from the Ti : sapphire laser. To measure the time-gated PL intensity at wavelength  $\lambda_F$ , the up-converted signal at the sum frequency  $c(\lambda_L^{-1} + \lambda_F^{-1})$  was spectrally filtered out by an interference filter (IF) with a bandwidth of 5 nm and detected with a cooled photomultiplier tube (PMT). The output pulses of the PMT were time-gated to enhance the signal-to-noise ratio. In this geometry, the detected PL showed no noticeable reduction in signal intensity over more than 60 min, i.e. on a time scale much longer than needed for a typical time-resolved PL measurement. The response function of this setup of about 250 fs was independently measured by detecting the second-harmonic radiation generated in a 3-hydroxypicolinic acid layer at 400 nm under similar excitation conditions. The response function is limited mainly by the dispersion of the MO. We primarily chose to use two-photon excitation in order to (i) suppress background signals and (ii) to achieve a higher spatial resolution to reduce the influence of possible sample inhomogeneities. Also, due to the large exciton binding energies in organic semiconductors of typically several hundred millielectronvolts, two-photon excitation gives access to one-photon-inactive exciton states with significant excess energy and possibly different relaxation dynamics, as has recently been studied in particular for carbon nanotubes [14, 15]. It would be interesting to explore these



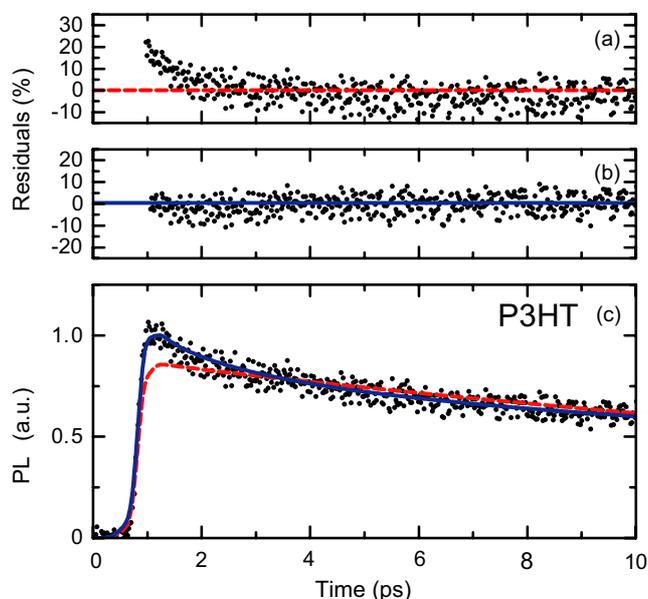
**Figure 2.** Absorption spectra of thin films of P3HT, PCBM and a P3HT : PCBM blend with a 1 : 1 weight ratio. Also shown is the PL spectrum of a pristine P3HT-film (dotted line) recorded after excitation with 15 ps laser pulses at a wavelength of 327 nm.

initial dynamics. Here, however, two-photon excitation with excess energies of more than 1 eV is chosen, and the initial exciton relaxation kinetics are too fast to be resolved in our experiments.

### 3. Results

The steady-state absorption and normalized PL spectra of 200 nm thick films of pristine P3HT show as the main feature characteristic absorption bands around 600 nm and emission bands around 640 nm with successive vibronic replicas on the high and low energy side, respectively (see figure 2). The energy positions and spectral shape of the different bands are as known for thin P3HT films from the literature and indicate the existence of weak intermolecular coupling [12, 16]. Also depicted in figure 2 are steady-state absorption spectra taken from spin-coated films of PCBM and from the 1 : 1 P3HT : PCBM blend. The spectrum of the blend can simply be approximated as the sum of the absorption spectra of the two constituents. At the two-photon excitation energy of 3.125 eV (corresponding to 400 nm excitation), both constituents in the blend contribute more or less equally to the total absorbance. The molecular weights of the two constituents are about  $50.000 \text{ g mol}^{-1}$  (mean value) and  $911 \text{ g mol}^{-1}$ , respectively. Taking a two-photon absorption cross section of  $0.2 \times 10^{-20} \text{ cm}^4 \text{ GW}^{-1}$  for P3HT, a typical value for the polymer 2-methoxy-5-(2'-ethylhexyloxy)-PPV (MEH-PPV) [17], we estimate that about 20% of the polymer chains in the laser focus are excited.

The PL decay traces of pristine P3HT and a 1 : 1 P3HT : PCBM blend recorded after two-photon excitation with 800 nm-laser pulses for a detection wavelength of 650 nm are shown in figures 3 and 4. Both traces reveal clearly nonexponential decays. The PL trace for the polymer film shows a rapid decay on a time scale of a few picoseconds. In the blend, a much faster PL decay occurs. The quenching is

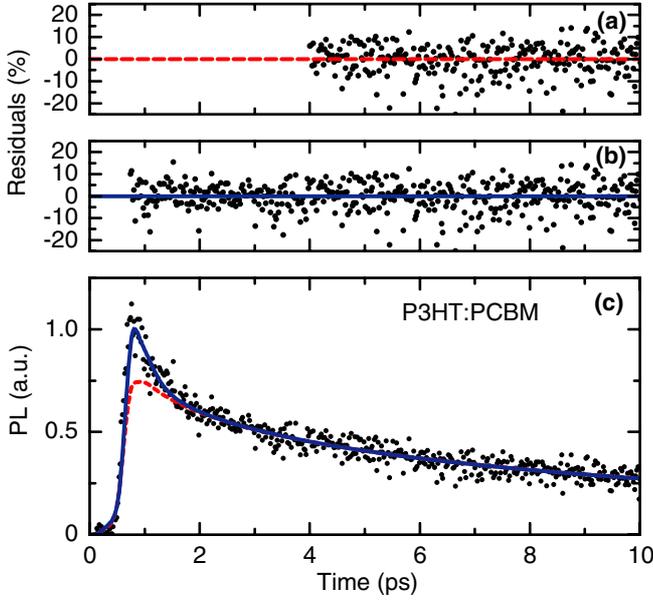


**Figure 3.** PL decay curve of pristine P3HT (closed circles in (c)) recorded at a detection wavelength of 650 nm after two-photon excitation with 800 nm laser pulses. The dashed line in (c) is a monoexponential fit to the data with a decay time of 26 ps. The corresponding weighted residuals are shown in (a). The solid line in (c) is a fit to the data representing a theoretical PL decay function introduced in the text which includes mobility and annihilation of excitons. The residuals of this approximation are shown in (b).

most pronounced within the first 1 or 2 ps, while the decay is also distinctly faster at later times.

### 4. Discussion

For a discussion of the measured decay traces, we start from the following scenario: the origins of the PL are electronic transitions from an excited state in the polymer which have a lifetime  $\tau_0$  when the transitions occur in single undisturbed chains. The initial exciton density  $N_0$  generated in the samples by the fs-laser pulses via two-photon excitation is roughly  $6 \times 10^{18} \text{ cm}^{-3}$ . This means that the excitons generated in the laser focus are on average spatially separated by 5.5 nm. Even though this density is lower than in many pump-probe experiments, it is sufficiently high to induce rapid exciton-exciton annihilation processes, which we include in the relaxation scenario with a rate  $k_{\text{EEA}}(t)$ . For the blend, i.e. in the presence of donor and acceptor moieties, also charge transfer processes have to be considered at a rate  $k_{\text{CT}}(t)$ . We essentially assume that the photogenerated excitons undergo a diffusive motion until they reach a certain minimum distance to the nearest neighbouring exciton,  $2R_0$ , or to the nearest acceptor molecule,  $2R_A$ . Once these interaction distances are reached, exciton-exciton annihilation or charge transfer occurs, respectively. In this scenario, the reaction rates for both processes are in general time-dependent and depend on the corresponding interaction distances as well as the exciton diffusion coefficient  $D$  [18]. Following these assumptions, we can write down the rate equation for the temporal development



**Figure 4.** PL decay curve of a P3HT : PCBM blend with 1 : 1 weight ratio (closed circles in (c)) recorded at a detection wavelength of 650 nm after two-photon excitation with 800 nm laser pulses. The lines in (c) are fits representing the PL decay models introduced in the text which exclude (dashed line) and include (solid line) an additional PL quenching assigned to prompt charge transfer. Also shown are the corresponding weighted residuals for an absence (a) and presence (b) of a fast PL quenching in the decay scenario.

of the exciton density  $N(t)$ :

$$\frac{dN}{dt} = -\frac{N}{\tau_0} - 2k_{\text{EEA}}(t) \frac{N^2}{N_0} - k_{\text{CT}}(t) N. \quad (1)$$

Its solution can be achieved by substituting  $M(t) = N(t)^{-1}$  and following the standard procedure for the emerging linear differential equation with an inhomogeneity.

Since exciton diffusion coefficients in conjugated polymers are comparatively small, the effect of the drift-diffusive exciton motion on the exciton relaxation is not particularly pronounced on a few picosecond time scale. Generally, here the root of the mean square displacement is less than the critical interaction radii  $R_0$  and  $R_A$  and it is sufficient to solve the rate equation (1) in the limit of isotropic and low diffusion. In this low-diffusion limit, the time-dependent rates for the charge transfer and the exciton–exciton annihilation can be written as  $k_{\text{CT}}(t) = \beta_1/\sqrt{t}$  and  $k_{\text{EEA}}(t) = \beta_2/\sqrt{t}$ , where  $\beta_{1,2} = 4R_{A,0}^2 N_{A,0} \sqrt{\pi D}$ , respectively. The parameters  $\beta_{1,2}$  depend quadratically on the specific interaction distances  $R_A$  or  $R_0$  for the respective process and show the same dependence on the acceptor density  $N_A$  or initial exciton density  $N_0$  and the exciton diffusion constant  $D$ . Substituting these rates into equation (1) leads to the general solution

$$N(t) = N_0 \left[ \exp\left(-\frac{t}{\tau_0} - 2\beta_1\sqrt{\tau_0}\right) \right] \times \left[ 4\beta_2\sqrt{\pi\tau_0} \exp(-\beta_1^2\tau_0) \times \left[ \text{erf}\left(\sqrt{\frac{t}{\tau_0}} + \beta_1\sqrt{\tau_0}\right) - \text{erf}\left(\beta_1\sqrt{\tau_0}\right) \right] + 1 \right]^{-1}. \quad (2)$$

Without charge transfer processes, i.e. in the limit  $k_{\text{CT}}(t) = 0$ , the temporal development of the exciton density  $N$  can be obtained with  $\beta_1 = 0$ .

To numerically simulate the measured PL decay traces, the exciton density  $N(t)$  according to equation (2) was convoluted with the instrumental response function and then fitted to the data points. The decay time  $\tau_0$  was generally fixed to a value of 575 ps as measured with dilute P3HT solutions using time-correlated single photon counting. A monoexponential decay model cannot adequately describe the data in figure 3. The weighted residuals for this model plotted in figure 3(a) show highly systematic deviations, giving evidence that processes like exciton–exciton annihilation indeed have to be taken into account when modelling the exciton relaxation in pristine P3HT. The decay time of only 26 ps obtained in the monoexponential fit is attributed to the considered time scale. For fitting the pristine P3HT data in figure 3 with our model, charge transfer processes are neglected ( $\beta_1 = 0$ ), whereas the parameter  $\beta_2$  was permitted to be varied. The best fit was obtained with  $\beta_2 = 2.8 \times 10^{-3} \text{ fs}^{-1/2}$  and the corresponding curve is presented in figure 3. The simulated decay describes the experimental data satisfactorily.

Having obtained  $\beta_2$  from the pristine P3HT sample, the data points of the P3HT : PCBM blend were then fitted with  $\tau_0$  and  $\beta_2$  being fixed to the values given above, while  $\beta_1$  was allowed to be varied. This procedure resulted in the dashed curve in figure 4 as the best fit with  $\beta_1 = 6.2 \times 10^{-3} \text{ fs}^{-1/2}$ . The simulated curve matches the data points, but only at times larger than 3 ps. Three conclusions can be drawn: (i) a monoexponential decay model neglecting exciton annihilation is inadequate for fitting the results for pristine P3HT as well as for the polymer blend. (ii) An additional, diffusion-controlled charge transfer channel needs to be assumed to match the experimental results for the blend at times larger than  $\sim 3$  ps. (iii) At shorter times, the experimental data deviate clearly from this diffusion-controlled annihilation/charge transfer model. To better describe the decay exciton density  $N(t)$  for  $t < 3$  ps, we have to assume that a certain fraction  $A_p$  of the photogenerated excitons can decay via an additional diffusion-independent charge transfer channel. This prompt charge transfer channel is put into the relaxation model by adding an exponential decay term with lifetime  $\tau_p$  and relative amplitude  $A_p$  to the right side of equation (2). The data were modelled by varying  $\beta_1$  together with  $\tau_p$  and  $A_p$ . A satisfactory fit was then obtained with  $\beta_1 = 6.6 \times 10^{-3} \text{ fs}^{-1/2}$ ,  $\tau_p = 150$  fs and a relative amplitude  $A_p$  of 50%. The corresponding curve is shown in figure 4 together with the residuals. This indicates that in the polymer blend about one-half of the photogenerated excitons are subject to a rapid nonradiative decay occurring on a timescale of  $\tau_p \simeq 150$  fs. We assign this rapid quenching of the PL to prompt charge transfer processes which occur quasi-instantaneously from photoexcited polymer chains to PCBM molecules located within the range of the characteristic interaction distance  $R_A$ . The relaxation rate is therefore time independent and the resulting time signature simply a monoexponential function.

Since the obtained value for  $\tau_p$  is close to the time resolution of our experiments, it should be considered with some care. Our experiments do, however, give a clear indication that, even in highly concentrated 1:1 polymer/fullerene blends, only a fraction of the photoexcited excitons undergoes this rapid charge transfer process. A significant fraction, about one half of the initially excited excitons, is unaffected by the prompt charge transfer and decay on a slower time scale, either by diffusion-controlled charge transfer processes or by exciton-exciton annihilation.

These first results highlight the sensitivity of the (sub-) picosecond decay of the polymer photoluminescence to various exciton relaxation phenomena, including diffusion-controlled exciton-exciton annihilation and charge transfer, but also to ultrafast charge transfer processes in polymer blends occurring on a 100 fs time scale before appreciable diffusive exciton motion can set in. Clearly, more experimental work is needed to gain more detailed information about the exciton dynamics in organic semiconductors via ultrafast photoluminescence studies. Excitation-density dependent studies of polymer blends with different mixing ratios should give insight into exciton diffusion processes. Spectrally and temporally resolved emission studies, for example, using ultrafast Kerr gating techniques [19], are desirable as they can provide important information about intrachain exciton energy relaxation processes. Finally, a combination of time-resolved photoluminescence with ultrahigh-resolution microscopy techniques promises access to the spatio-temporal exciton dynamics in organic optoelectronic devices.

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