

Relation between exciplex formation and photovoltaic properties of PPV polymer-based blends

Chunhong Yin^a, Thomas Kietzke^{a,b,*}, Michael Kumke^c,
Dieter Neher^a, Hans-Heinrich Hörhold^d

^a*Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany*

^b*Institute of Materials Research and Engineering (IMRE), Research Link 3, 117602 Singapore, Singapore*

^c*Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Street 24-25, 14476 Golm, Germany*

^d*Institute of Organic Chemistry and Macromolecular Chemistry, University of Jena, Humboldtstr. 10, 07743 Jena, Germany*

Available online 5 December 2006

Abstract

As a new record for pure polymer-blend solar cells, an energy conversion efficiency (ECE) of 1.7% was recently achieved for M3EH-PPV:CN-ether-PPV (Poly[oxa-1,4-phenylene-1,2-(1-cyano)-ethylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)-ethylene-1,4-phenylene]) based devices [T. Kietzke, H.-H. Hörhold, D. Neher, *Chem. Mater.* 17 (2005) 6532]. Even though that photoluminescence experiments indicated that 95% of the photogenerated excitations were dissociated in the blend, the external quantum efficiency reached only 31%. Thus more than 2/3 of the dissociated excitons were lost for the energy conversion. In order to identify the processes which limit the photovoltaic efficiency of polymer-blend solar cells, studies on the steady state and time-resolved photoluminescence of the individual polymer and polymer blend were performed. In the polymer-blend layer, we observed a considerable long-wavelength emission due to exciplex formation. The exciplex emission can be reduced by thermal annealing. At the same time the IPCE of the blend-based device increased, indicating a more efficient generation of free-charge carriers. These findings lead to the conclusion that charge-carrier recombination via exciplex formation constitutes one of the loss channels which limits the efficiency of polymer solar cells.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Polymer blends; Exciplex; Solar cells; PPV; Time-resolved photoluminescence

1. Introduction

Photovoltaic devices based on blends of semiconducting polymers exhibited high external quantum efficiencies [1–5]. It is well established that by using heterojunctions of donor and acceptor, the dissociation of the photo-generated excitons into charge carriers is improved. Currently, organic photovoltaic devices based on blends of conjugated polymers like polythiophenes (PT) or polyphenylenevinylene (PPV) derivatives and the functionalised fullerene derivative PCBM as electron acceptor reached external quantum efficiencies exceeding 70% [6–8]. However, these devices consist of up to 80 wt% of

PCBM and the strong acceptor strength of PCBM limits the open-circuit voltages to below 0.9 V. Contrary, for polymer–polymer blends open-circuit voltages even exceeding 1.5 V have been reported, but due to the smaller fill factor and the lower short-circuit current the energy efficiencies could not exceed 1.7% so far. This efficiency could be achieved by blending M3EH-PPV (poly[2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylenevinylene-1,2-ethenylene)]) [9] as electron donor and CN-ether-PPV (poly[oxa-1,4-phenylene-1,2-(1-cyano)-ethylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)-ethylene-1,4-phenylene] [10]) as the electron-accepting component. M3EH-PPV can be regarded as a strictly alternating copolymer of the soluble MEH-PPV and the insoluble 2,5-dimethoxy-PPV. Here, we are presenting detailed spectroscopic investigations on the blend and the pure polymers to identify the principal process limiting the device efficiency and try to

*Corresponding author. Institute of Materials Research and Engineering (IMRE), Research Link 3, 117602 Singapore, Singapore.
Tel.: +65 68727546; fax: +65 68727528.

E-mail address: k-thomas@imre.a-star.edu.sg (T. Kietzke).

identify the mechanism, which leads to increase in efficiency after annealing the device.

2. Experimental methods

2.1. Preparation

For the solar cells, an approximately 50 nm thin layer of poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) was spin coated onto commercially available glass substrates covered with indium tin oxide (ITO, 13 Ω /square). Then, the PEDOT:PSS films were dried on a hot plate under nitrogen atmosphere for 30 min at 110 °C. M3EH-PPV and CN-Ether-PPV were dissolved in a 1:1 weight ratio in chlorobenzene. After coating the blend the layers were annealed in nitrogen atmosphere at 110 °C for 30 min. The devices were completed by evaporating a 20 nm Ca layer protected by 100 nm Al. The effective solar-cell area as defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 0.20 cm². All device preparation and characterization were performed under nitrogen atmosphere (Fig. 1).

For the spectroscopic measurements the layers were coated on glass substrates, followed for some samples by an annealing step at 110 °C. To avoid degradation from oxygen and water, a 200 nm thick silver layer was evaporated on the polymer layers and the samples were encapsulated using a second glass slide.

Device characterization: The external quantum efficiency (IPCE) as a function of wavelength was measured with an Oriel 150 W Xe-lamp in combination with an Oriel Cornerstone 260 monochromator. The number of photons incident on the device was calculated at each wavelength by using a calibrated Si-diode as reference.

2.2. Spectroscopy

Steady-state fluorescence spectra were measured with Perkin-Elmer LS 55 luminescence spectrometers. The time-resolved photoluminescence was measured by using a single photon-counting setup. For the excitation of the samples a frequency-doubled titanium:sapphire laser (Tsunami, Spectra Physics) was used. The excitation pulse width was determined to 100 fs by using an autocorrelator (Pulse Check, APE, Berlin). Fluorescence spectra were measured with a FL920 fluorometer (Edinburgh Instru-

ments, Livingston, UK). The complete detection system had an instrumental response time of 100 ps. For data analysis and deconvolution of the instrument-response function, the commercial software package provided with the FL920 fluorescence spectrometer was used.

3. Results and discussion

3.1. Steady-state photoluminescence studies

Efficient exciton dissociation at the donor–acceptor heterojunction in conjugated polymer systems is a requirement for efficient polymer photovoltaic devices. Comparing the photoluminescence efficiency of a layer of M3EH-PPV with that of a 1:1 M3EH-PPV:CN-Ether-PPV blend layer provides information on the exciton dissociation efficiency. If the excitons are efficiently dissociated, direct exciton recombination is suppressed and thus the photoluminescence emission is quenched.

Surprisingly the PL of the M3EH-PPV:CN-ether-PPV blend is quenched to about 5% of the pure M3EH-PPV layer emission indicating that 95% of the excitons are dissociated (Fig. 2). Thus CN-ether-PPV as electron acceptor combined with M3EH-PPV is nearly as efficient as the well-studied PCBM.

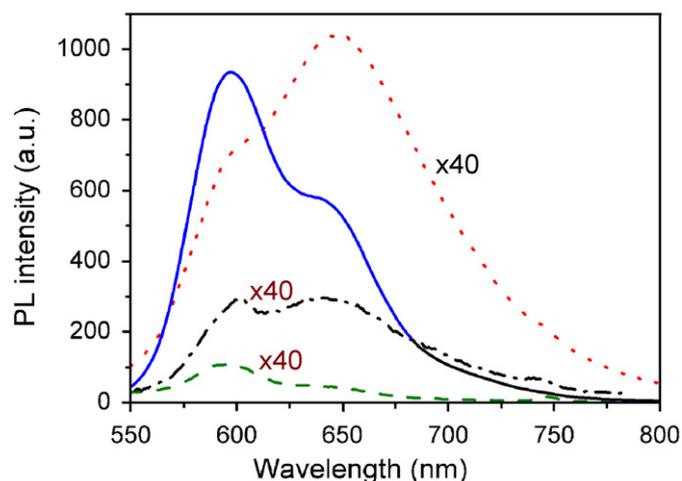


Fig. 2. The PL spectra of a M3EH-PPV layer (solid line) and of a 1:1 (by weight) blend layer of M3EH-PPV:CN-ether-PPV before (dotted line) and after annealing (dashed dotted) and of M3EH-PPV:PCBM (dashed line), respectively.

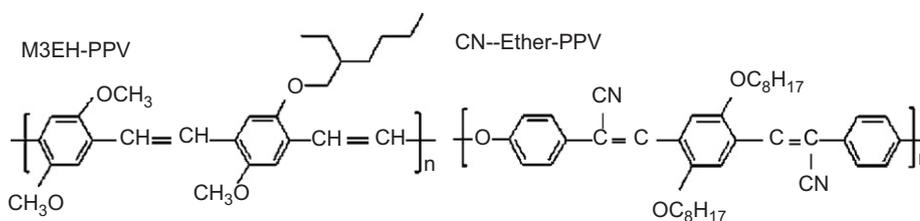


Fig. 1. The chemical structures of M3EH-PPV and CN-ether-PPV.

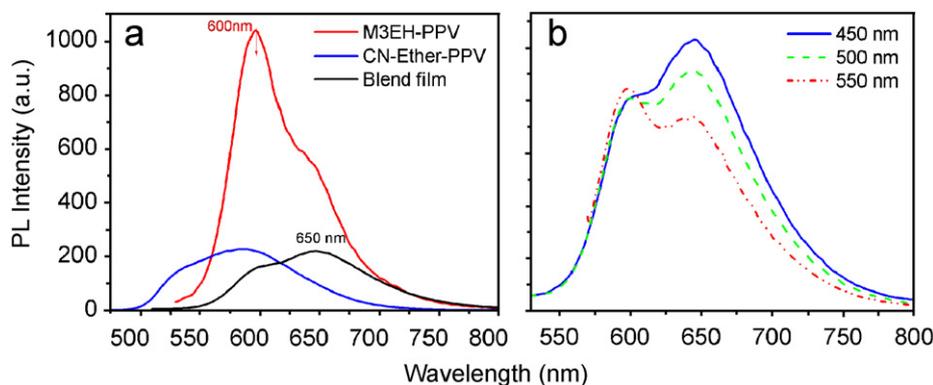


Fig. 3. (a) The PL spectra of M3EH-PPV, CN-ether-PPV neat films and of a 1:1 (weight ratio) blend film of these two polymers. The excitation wavelengths were chosen at the maximum absorbance and (b) the PL spectra of M3EH-PPV:CN-ether-PPV blend film excited at different wavelengths.

Comparing the PL spectra of the pure layer and the blend layer (Fig. 3), one can find a new feature at 650 nm, which is present neither in the emission of the pure-polymer layers, nor in the spectrum of a 1:1 blend of M3EH-PPV and PCBM. After changing the excitation wavelength from 450 nm (excitation mostly of CN-ether-PPV) to 550 nm (excitation solely of M3EH-PPV), the 650 nm emission still remained and the PL intensity at this wavelength did not change significantly (Fig. 3b). All the observations indicate that a new emitting species is formed in the blend film.

In order to resolve the nature of the 650 nm emission, time-resolved spectroscopy studies with a single photon-counting setup were performed.

3.2. Time-resolved photoluminescence studies on neat polymer films and polymer blend

For the time-resolved measurements two set of samples, a layer of M3EH-PPV and a layer of M3EH-PPV:CN-ether-PPV blend (1:1), were prepared on glass. One set was annealed at 110 °C, the other was measured as prepared. The excitation wavelength was fixed at 400 nm due to experimental conditions. At this wavelength, both CN-ether-PPV and M3EH-PPV can be excited. All recorded transients showed a multi-exponential decay, which could be fitted with either two or three exponential functions.

3.2.1. Studies on pure M3EH-PPV layer

The pure M3EH-PPV layer shows the fastest decay with a time constant considerably below 0.8 ns for both the emission at 600 and 650 nm, as shown in Fig. 4. This short-time scale is typical for intra-chain recombination in conjugated polymers [11,12]. The decay time is relatively insensitive to the emission wavelength. Thus, there is no indication that more than one emitting species is presented.

3.2.2. M3EH-PPV CN-ether-PPV: blend

In the transients of the as-prepared blend layers shown in Fig. 5, two decay channels could be identified: a fast decay with decay time below 0.4 ns and two longer components

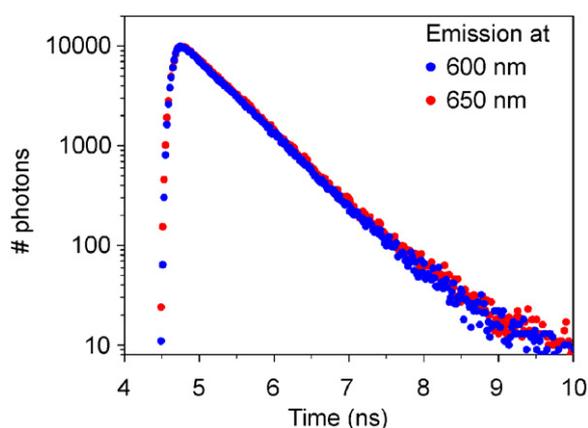


Fig. 4. Time-resolved transients of a M3EH-PPV layer excited at 400 nm. The decay time is faster than 0.8 ns.

with decay times of 2 ns and 5.5 ns as shown by the fit parameters in Table 1.

This leads to the conclusion that the emission at 600 nm is caused by recombinations of excitons on M3EH-PPV while the emission at 650 nm involves inter-chain processes.

3.3. Exciplex emission and device performance upon annealing

Annealing at 110 °C did not influence the decay times for the pure M3EH-PPV and CN-ether-PPV layers, but a significant change was found for the blend layer. After annealing, the component of fast emission decay at 600 nm increased to 85%. Also the 650 nm emission was now dominated by this short component. In addition, for the steady-state measurements, the absolute PL of the blend at 650 nm decreased after annealing, in contrast to the PL of CN-ether-PPV, which increased after annealing (as shown in Fig. 6). This PL increase is probably due to a better packing of the chains. Finally, steady-state excitation spectra recording the 650 nm emission in the blend films (not shown here) clearly resembled the absorbance of both CN-ether-PPV and M3EH-PPV.

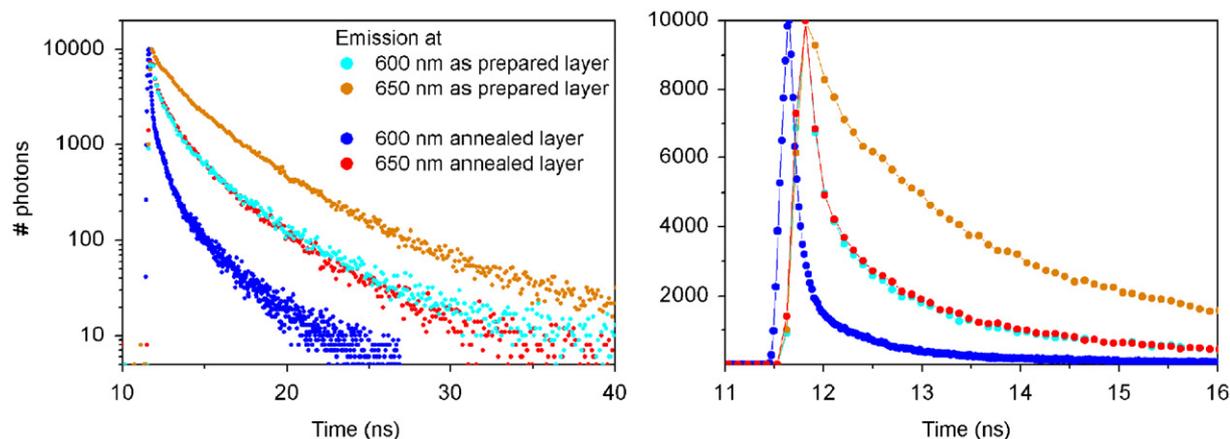


Fig. 5. Time-resolved transients of a M3EH-PPV:CN-ether-PPV blend layer excited at 400 nm before and after annealing at 110 °C.

Table 1
Fluorescence-decay times for the M3EH-PPV:CN-ether-PPV blend layer obtained by the best fit

Emission	600 nm		650 nm	
	As prepared	110 °C annealed	As prepared	110 °C annealed
Dominant τ	0.35 ns (52%)	0.07 ns (71%)	2.2 ns (57%)	0.4 ns (63%)
	1.9 ns (26%)	0.9 ns (14%)	5.8 ns (34%)	1.7 ns (27%)
	5.5 ns (12%)	2.9 ns (15%)	0.23 ns (9%)	4.9 ns (10%)

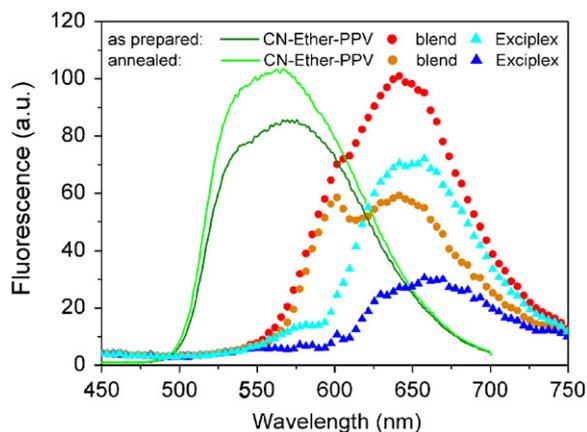


Fig. 6. The steady-state photoluminescence of CN-ether-PPV and the CN-ether-PPV:M3EH-PPV blend of a as-prepared layer and a layer annealed at 110 °C. The excitation took place at 400 nm. The exciplex component (triangles) was obtained by subtracting the remaining M3EH-PPV emission.

From these findings it seems reasonable to attribute the 650 nm emission in the blend to the formation and recombination of an exciplex formed between M3EH-PPV and CN-Ether-PPV chains. This exciplex forms in less than 1 ns, which is below the time needed to form an excimer in CN-ether-PPV as demonstrated before.

This idea of the exciplex formation in PPV-based blends can help to explain why 95% of the excitons dissociate at the donor-acceptor interface as obtained from the quenching experiments but only 30% reach as free carriers the

electrodes. Following the ideas first proposed for a blend of polyfluorene derivatives (PFB:F8BT) we suggest that after dissociation of the excitons no free-charge carriers, but the so-called geminate pairs are formed [13,14]. These geminate pairs will then either recombine via exciplex emission or nonradiatively recombination and only a fraction will further dissociate into completely free-charge carriers. The exciplex contribution to the overall blend emission can be deconvoluted. We found that after annealing the exciplex contribution decreased by a factor slightly larger than two. At the same time the device efficiency increased by a similar factor as shown in Fig. 7.

Most likely, the annealing step induced a larger phase separation of the polymers leading to reduced interchain interactions.

4. Summary

We have reported on detailed investigations on the PL dynamics of the CN-ether-PPV and M3EH-PPV homopolymers as well as of the 1:1 blend of both polymers. We found that in the blend photogenerated excitons are efficient separated as shown by the nearly complete PL quenching. However, time-resolved spectroscopy measurements proved the existence of a new emitting species in the blend, which we attribute to be an exciplex. We found a clear correlation between the quenching of exciplex emission and the IPCE of the solar cells. Upon annealing, the exciplex emission is reduced while at the same time the IPCE increases, indicating a more efficient generation of

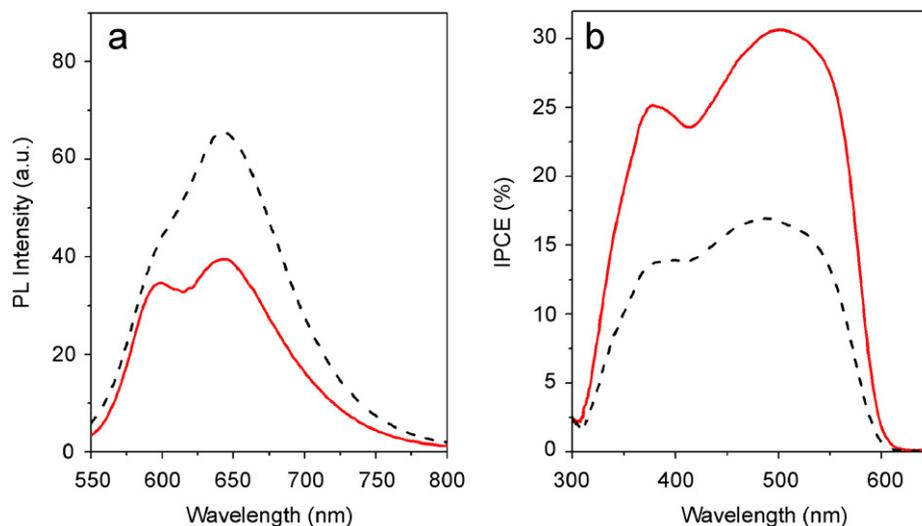


Fig. 7. The correlation between the exciplex emission and device efficiency in M3EH-PPV:CN-ether-PPV blend devices: (a) the PL spectra of blend layer of M3EH-PPV:CN-ether-PPV (1:1 by weight) before (dashed line) and after annealing at 110 °C for 30 min (solid line), respectively and (b) the corresponding IPCE spectra. The device structure was as follows: glass/ITO/PEDOT:PSS (40 nm)/PPV blend (55 nm)/Ca/Al.

free-charge carriers. These findings lead to the conclusion that charge-carrier recombination via exciplex formation constitutes one major loss channels which limits the efficiency of polymer solar cells.

Acknowledgements

We thank the Volkswagenstiftung for their financial support.

References

- [1] T. Kietzke, H.-H. Hörhold, D. Neher, *Chem. Mater.* 17 (2005) 6532.
- [2] G. Yu, A.J. Heeger, *J. Appl. Phys.* 78 (1995) 4510.
- [3] G. Yu, J. Gao, J.C. Hummelen, et al., *Science* 270 (1995) 1789.
- [4] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 15.
- [5] A.J. Breeze, Z. Schlesinger, S.A. Carter, et al., *Sol. Energy Mater. Sol. Cells* 83 (2004).
- [6] C.J. Brabec, *Sol. Energy Mater. Sol. Cells* 83 (2004) 273.
- [7] H. Hoppe, N.S. Sariciftci, *J. Mater. Res.* 19 (2004) 1924.
- [8] M.M. Wienk, J.M. Kroon, W.J.H. Verhees, et al., *Angew. Chem.Int. Edit.* 42 (2003) 3371.
- [9] S. Pfeiffer, H.-H. Hörhold, *Macromol. Chem. Phys.* 200 (1999) 1870.
- [10] H. Tillmann, H.-H. Hörhold, *Synth. Metals* 101 (1999) 138.
- [11] L. Smilowitz, A. Hays, A.J. Heeger, et al., *J. Chem. Phys.* 98 (1993) 6504.
- [12] M. Yan, L.J. Rothberg, E.W. Kwock, et al., *Phys. Rev. Lett.* 75 (1995) 1992.
- [13] A.C. Morteani, A.S. Dhoot, J.-S. Kim, et al., *Adv. Mater.* 15 (2003) 1708.
- [14] A.C. Morteani, P. Sreearunothai, L.M. Herz, et al., *Phys. Rev. Lett.* 92 (2004) 247402.