

Ultrafast spectroscopy of polaron pairs in polymer solar cells

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Abstract

We use a femtosecond two step photocurrent technique to study the role of bound polaron pairs during charge carrier generation in two different conjugated polymer/fullerene blend systems. In pure MeLPPP and in pure MDMO-PPV polaron pairs are formed and can be dissociated via reexciting with a second laser pulse tuned to the respective polaron absorption band. When blended with a fullerene, however, bound polaron pairs are only formed in MeLPPP/PCBM while they do not play a role in the PPV sample.

Keywords: Time-resolved fast spectroscopy; Amorphous thin films; Poly(phenylene vinylene) and derivatives; Fullerene and derivatives; Detectors; Solar cells

1. Introduction

Conjugated polymers bear a large potential for applications in large-area photodetectors and solar cells. In these devices the highly absorbing conjugated polymer is blended with a high electron affinity material, e.g. fullerene derivatives. The underlying process in such photocells is a photoinduced electron transfer from the initially excited conjugated polymer to the electron acceptor. This process can be ultrafast and occurs with high quantum yield, even for moderate acceptor concentrations. The resulting pair of oppositely charged carriers can then either remain weakly bound and form a polaron pair [1] or fully dissociate into two mobile charges. The energetics and dynamics of polaron pair formation, dissociation and recombination is currently intensely investigated [2].

In this paper we combine ultrafast optical techniques with photocurrent measurements to compare two different blends of a conjugated polymer and an electron accepting fullerene derivative (PCBM). The first sample uses a poly(phenylene-vinylene) (MDMO-PPV) as the polymeric component. This combination has recently been used for the preparation of polymer solar cells with efficiencies exceeding 3 % [3]. For the second sample we use a methyl-substituted ladder-type poly(*p*-phenylene) (MeLPPP), a polymer that has been used for the preparation of high

efficiency LEDs and low threshold organic lasers. Both polymers have similar optical properties and hole mobilities. When blended with PCBM the photoluminescence is in both samples drastically quenched by more than 95 % indicating an efficient electron transfer in both materials. The quantum efficiency for the photocurrent generation, however, is a factor of 5 lower for the sample made of MeLPPP. Using femtosecond two step charge carrier generation experiments we show that this difference can be attributed to the formation of bound polaron pairs in MeLPPP/PCBM while these Coulombically bound species does not play a role in MDMO-PPV/PCBM.

2. Experimental

In our fs-experiments we use a regeneratively amplified Ti:sapphire-laser with a repetition rate of 1 kHz and a pulse duration of 120 fs. Frequency doubled pulses with a photon energy of 3.1 eV are used to excite the sample. The second laser pulse is derived from an optical parametric amplifier pumped by the same amplified Ti:sapphire-laser. For both samples the second laser pulse is tuned to the polaronic photoinduced absorption band in the different polymers, i.e. 1.91 eV in MeLPPP and

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1.30 eV in MDMO-PPV. For these photon energies the ground state absorption is in both polymers negligible. We then measure the changes $\Delta PC/PC$ of the time integrated photocurrent at zero bias induced by the second laser pulse as a function of the time delay between the first and the second laser pulse.

The samples are sandwich-type structures, prepared by spincoating a solution containing both the donor and the acceptor component onto an indium-tin-oxide (ITO)-coated glass substrate additionally covered with PEDOT. Toluene is used as the common solvent. The thickness of the organic layer is about 150 nm. The diode structure is completed by evaporating an aluminum contact.

2. Results

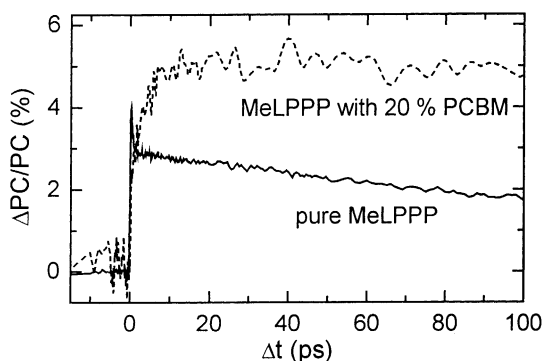


Fig. 1. Transient photocurrent changes induced by the second laser pulse in the MeLPPP layer with and without fullerene. For excitation a laser pulse at 3.1 eV is used. The second laser pulse is tuned to the polaron absorption band at 1.91 eV.

Figure 1 shows the $\Delta PC/PC$ transients for the pure MeLPPP and the same polymer blended with the fullerene. In both cases a strong photocurrent increase is observed when the 1.91 eV laser pulse impinges the samples after photoexcitation with the 3.1 eV laser pulse. The first laser pulse generates vibronically excited S_1 -excitons. Some of them spontaneously form polaron pairs that can subsequently dissociated by reexcitation with a second laser pulse tuned to the polaron absorption band [4]. A similar and even more pronounced effect is observed for the fullerene containing sample. After photoexcitation polaron pairs with the positive charge located on the polymer and the electron located on the fullerene are formed. With the second laser pulse these pairs can be dissociated into mobile charges and concomitantly contribute to the photocurrent. The observed delayed signal rise in the fullerene-containing sample is attributed to the

delayed formation of polaron pairs out of the initially excited S_1 -excitons in MeLPPP.

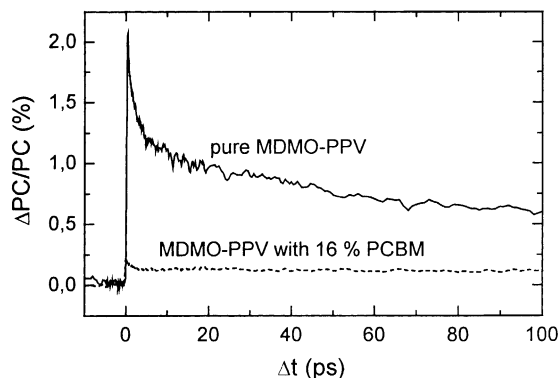


Fig. 2. Transient photocurrent changes induced by the second laser pulse for the MDMO-PPV samples. For excitation a laser pulse at 3.1 eV is used. The second laser pulse is tuned to the polaron absorption band at 1.91 eV.

Fig. 2 displays the results for the samples using MDMO-PPV as the semiconducting polymer. In case of the pure polymer sample again a strong photocurrent increase is observed. As in MeLPPP it can be attributed to the reexcitation of loosely bound geminate polaron pairs, which are excited to higher lying states with high dissociation probability. In contrast to the case of MeLPPP the signal amplitude is drastically decreased upon adding 16 % PCBM. We attribute this to a vanishing density of bound polaron pairs in MDMO-PPV/PCBM. In agreement with the much higher photocurrent efficiency in this material bound polaron pairs are either not formed at all or they are not a stable species. We speculate that a larger delocalization of the excited state in MDMO-PPV also leads to a larger typical distance and thus a smaller Coulombic attraction between the hole and the electron after the initial electron transfer.

In conclusion we have used a femtosecond two step photocurrent technique to study the role of bound polaron pairs during charge carrier generation in conjugated polymer/fullerene blend systems. Both, in pure MeLPPP and in pure MDMO-PPV polaron pairs are formed and can be dissociated via reexciting with a second laser pulse tuned to the respective polaron absorption band. When blended with a fullerene, however, in MDMO-PPV the role of bound polaron pairs is negligible while they are important in the case of MeLPPP.

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