

Polaron dynamics in thin polythiophene films studied with time-resolved photoemission

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Received: date / Revised version: date

Abstract Femtosecond time-resolved two-photon photoemission spectroscopy is employed to study the dynamics of an excited state in a thin regioregular poly(3-hexylthiophene) (RR-P3HT) film deposited on a conducting polymer poly(3,4-ethylene-dioxythiophene): poly-(styrenesulfonate) (PEDT:PSS) electrode following optical excitation at 2.1 eV. We found that the biexponential decay of this excited state has a fast component (2.6 ps) assigned to bound polaron pairs which recombine quickly or separate to be added to the slow component (7.6 ps). The latter is attributed to polarons generated *via* charge transfer between adjacent polymer chains.

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1 Introduction

Organic photovoltaic cells (OPVC) are one of the most auspicious alternative for traditional silicon-based solar cells [1], [2]. This new generation of solar cells is fabricated using either small molecules or polymers as active semiconductor layers. The latter are favored because of their higher potential for real low cost and large area production as thin homogenous polymer films can be easily made from solution. The best performances for polymer based OPVCs are obtained using regioregular poly(3-hexylthiophene) (RR-P3HT) as donor material (up to $\approx 5\%$ efficiency [3]) and poly(3,4-ethylene-dioxythiophene): poly-(styrenesulfonate) (PEDT:PSS) (see Fig. 1) is the electrode of choice for almost all OPVCs due to its transparency in the visible spectrum [4], its high conductivity [5] and work function. In P3HT electrons are usually delocalized on the π -conjugated backbone of the polymer, resulting in a high conductivity in the organic film, which can be increased up to 1000 S/cm when doped with iodine [5]. In this work we are using regioregular RR-P3HT showing self-organization of the chains into a lamellae structure resulting in relatively strong interchain interactions compared to regiorandom (RRa) P3HT that keeps a more chainlike morphology in the film.

In order to optimize device performance, good knowledge of the electronic properties of the polymers is needed. In this study we utilized time-resolved two-photon photoemission (2PPE) in order to gain insight into the excited states dynamics in the polymer film deposited on PEDT:PSS.

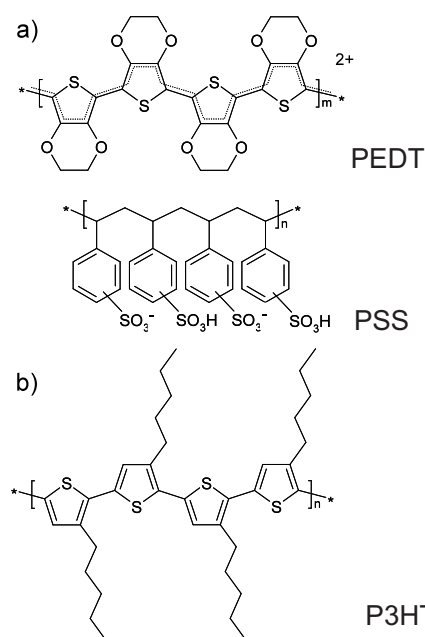


Fig. 1 Chemical structure of a) the conducting polymer mixture PEDT:PSS and b) P3HT.

At present, studies on the dynamics of electronic excitations and charge transfer processes at the adsorbate/substrate interface are limited to rather simple molecular systems (small molecules) adsorbed on single crystal metal or semiconductor surfaces [9], [10], [11], [13], [12], [14], [15], [16], [17], [18], [19]. In the literature only a few 2PPE studies using nanosecond laser pulses on conjugated polymer films on metal substrates [20], [21] exist. However, interfaces of direct relevance to OPVCs, i.e., conjugated polymer/ polymer electrode have so far not been addressed. Here we show that 2PPE is a suitable tool to probe excited states dynamics in thin polymer films, namely the polaron dynamics in thin P3HT films.

2 Experimental

Two-photon photoemission spectroscopy: The experimental setup combines a tunable femtosecond laser system with an ultrahigh vacuum (UHV) chamber for time-resolved two-photon photoemission spectroscopy and surface science techniques. For the 2PPE measurements, femtosecond laser pulses are generated by a 300 kHz Ti:Sapphire laser system which pumps an optical parametric amplifier (OPA). The visible output with photon energies between 1.7 eV and 2.7 eV is frequency doubled to generate ultraviolet pulses. The frequency doubled pulses $h\nu_2$ and the visible fundamental $h\nu_1$ are delayed with respect to each other (pump and probe pulse) and focused onto the sample. Thereby a pulse duration of around 60 fs is achieved [18]. While the pump pulse excites an electron from below the Fermi level E_F to intermediate unoccupied states at energies $E = E_{kin} + \Phi - h\nu_2$ (with Φ the work function), the probe pulse photoionizes the sample by lifting the electron above the vacuum level (E_{vac}). Photoelectrons are detected in an electron time-of-flight (TOF) spectrometer and analyzed with respect to their kinetic energy E_{kin} . The energy resolution of the TOF spectrometer depends on the electron energy, in the range of $E_{kin} \approx 1$ eV it is around 20 meV.

Film preparation: As substrates indium-tin-oxide (ITO) coated glass substrates (sheet resistance 15-30 Ω) were used. ITO samples were cleaned by ultrasonication in acetone and isopropanol. PEDT:PSS (AI4083, H.C. Stark GmbH and Co. KG) was deposited by spin coating at 1500 rpm and

dried at 200 °C for 5 min at ambient atmosphere. P3HT (Aldrich $M_n \sim 64.000$) was spin coated (3000 rpm) in inert atmosphere from chloroform solution with various concentrations (0.5 mg/ml, 1 mg/ml and 2 mg/ml).

3 Results and Discussion

In the following we discuss the results on the charge carrier dynamics in thin regioregular RR-P3HT films on PEDT:PSS obtained by time-resolved 2PPE. In Figure 2, a false color representation of the photoemission intensity of a 24 nm RR-P3HT film on PEDT:PSS recorded with photon energies of $h\nu_1 = 2.1$ eV for the visible and $h\nu_2 = 4.2$ eV for the UV laser pulses represents the electron distribution as a function of both time delay (horizontal axis) and energy (vertical axis). Depending on the sequence of laser pulses (or formally the sign of the pump-probe delay), the electrons are probed either near E_F or at higher intermediate state energies. Negative delays correspond to populating intermediate electronic states with UV light pulses ($h\nu_2$), while the visible pulses ($h\nu_1$) subsequently probe the excited electron distribution. On the other hand, for positive delays the electrons are excited to intermediate states close to the Fermi level (hot electrons) with the visible pulses ($h\nu_1$) and are subsequently probed by the UV pulses ($h\nu_2$). Analyzing the two-dimensional data set by extraction of the time-dependent 2PPE photoelectron yield integrated over the energy intervals centered on the state of interest, e.g. unoccupied intermediate state labeled

as A, provides the temporal evolution of the electron population, referred to as cross correlation traces as shown in the bottom panel of Fig. 2.

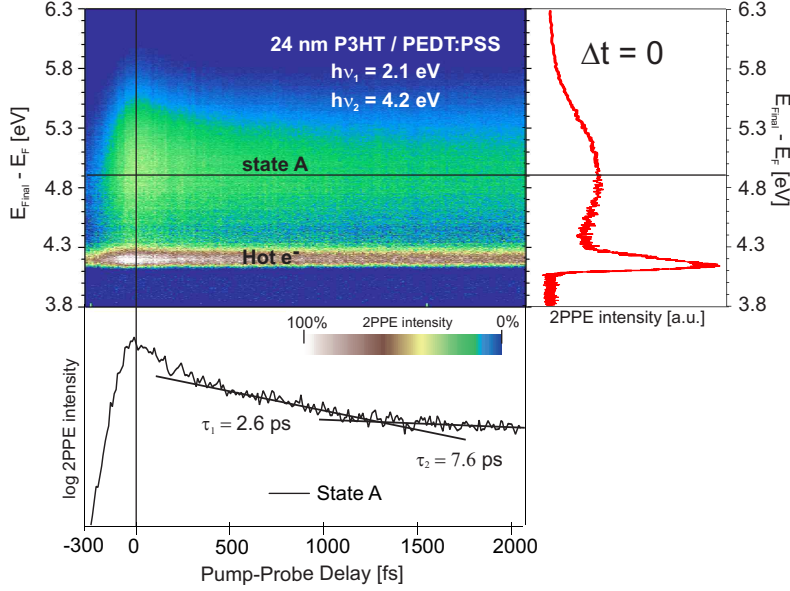


Fig. 2 2D-plot of 2PPE spectra as a function of pump-probe delay of a 24 nm P3HT film on PEDT:PSS. For positive delays, the VIS pulse ($h\nu_1 = 2.1$ eV) arrives at the surface before the UV pulse ($h\nu_2 = 4.2$ eV), therefore the unoccupied intermediate state labeled as state A is VIS-pumped and UV-probed. The spectrum on the right corresponds to a cut at zero time delay. The bottom panel shows cross correlation trace for the energy region of state A.

A broad photoemission feature located around $E_{Final} - E_F = 4.9$ eV is observed labeled as A showing a lifetime towards positive pump-probe delay. Hence this unoccupied intermediate state is pumped by the visible photons ($h\nu_1 = 2.1$ eV) and probed by the UV pulses ($h\nu_2 = 4.2$ eV) therefore its energetic position is ~ 0.7 eV above E_F (note that the energy scale is refer-

enced to the Fermi level of PEDT:PSS). The cross correlation trace for the energy region of state A is shown in the bottom panel of Fig. 2. Fitting the cross correlation trace with a biexponential decay results in time constants of 2.6 ps and 7.6 ps. In order to assign this unoccupied intermediate state we have to consider both its energetic position and lifetime. From UPS measurements it is known that the upper valence band (VB) edge of P3HT is located 0.2 eV below the Fermi level of PEDT:PSS [22]. Surprisingly we do not observe the bottom edge of the conduction band in the 2PPE spectrum. However the commonly accepted optical band gap of P3HT is 1.9-2.1 eV [23]. Thus the unoccupied state labeled as A which we observe in the 2PPE is located 0.9 eV above the VB edge (see Fig. 3), corresponding to 1.0-1.2 eV below the bottom edge of the conduction band (CB).

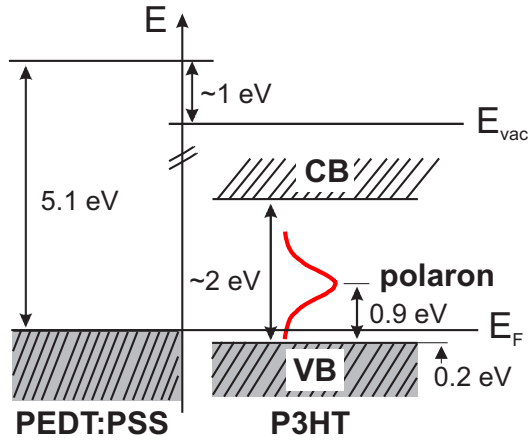


Fig. 3 Energetic position of the polaron in P3HT observed in the present study.

The Fermi level of PEDT:PSS serves as reference.

It is known that the photoexcitation of π -electrons with photon energies greater than the band gap of P3HT will induce the formation of excitons [25]. An exciton can either meet another exciton and undergo exciton-exciton annihilation or decay to the ground state. Moreover, if the exciton is created close to a dissociation center, for instance another polymer chain, it can undergo a charge transfer and produce a bound polaron pair with the negative and positive polaron on adjacent chains. Ruseckas *et al.* [26] have reported that this process is very efficient in polythiophene and takes place within 100 fs after photoexcitation. This bound polaron pair can recombine, be trapped by a defect state or dissociate into two charge carriers.

The binding energy of the exciton in RR-P3HT reported by Sakamoto *et al.* [25] is 0.7 eV and its lifetime is in the order of a few hundred femtoseconds [27]. Moreover it is known from literature that two delocalized polaron bands located at 0.1 eV and 1.85 eV, as well as two localized polaron bands at 0.35 eV and 1.25 eV, respectively, are existent in RR-P3HT [24], *viz.* in the energy regime where we find the broad 2PPE feature. Therefore we assign the fast component (2.6 ps) to bound polaron pairs, in which positive and negative polarons are bound to each other on adjacent chains by Coulomb interaction. The bound polaron can recombine quickly or separate and be added to the slow component (7.6 ps) assigned to polarons generated by charge transfer between adjacent polymer chains. Due to electronic and geometric disorder in the P3HT films, the broadening of the polaron peak does not allow to differentiate energetically the polarons from the bound

polaron pairs. Note that, varying the film thickness from 5 nm to 30 nm did not lead to significant changes in the polaron dynamics. In order to support our assignment a comparison between the observed charge carrier dynamics in RR-P3HT films forming a lamellae structure with non negligible interchain interactions and the dynamics in regiorandom (RRa) P3HT films keeping a chainlike morphology could certainly be useful to gain further insight into the nature of the observed processes. However, our study shows that time-resolved 2PPE is a powerful tool to investigate the excited state dynamics in polymer films.

Acknowledgments

Funding by the Deutsche Forschungsgemeinschaft (DFG) through the priority program SPP 1355 "Elementary Processes in Organic Photovoltaics" is gratefully acknowledge.

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