Tracing photoinduced electron transfer process in conjugated polymer/fullerene bulk heterojunctions in real time

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Abstract

Ultrafast spectroscopic studies using an optical excitation of a conjugated polymer by sub-10-fs pulses are reported. Phonon modes which are strongly coupled to the electronic excitation of the conjugated polymer are directly observed as coherent oscillations during the pump–probe experiment, mirroring the resonant/nonresonant Raman spectrum of the conjugated polymer. In composites of a conjugated polymer with a fullerene the primary photoexcitation is found to be an ultrafast photoinduced electron transfer. We are able to time resolve for the first time the kinetics of this charge transfer process with a forward transfer time of around $\tau_{ct} \sim 45$ fs. © 2001 Elsevier Science B.V. All rights reserved.

Photoinduced electron transfer in organic molecules is an intensively investigated topic in physics, chemistry and biology [1], both for the fundamental interest in the photophysics of excited states and for providing a synthetic approach to a deeper understanding of solar energy conversion in green plants. The discovery of a very efficient photoinduced electron transfer from conjugated polymers to Buckminsterfullerene (C_{60}) [2,3] opened up a new research direction with potential applications to photovoltaics, nonlinear optics and artificial photosynthesis. While in such composites the forward electron transfer time is

remarkably fast, the backtransfer is heavily hindered, resulting in metastable charge separated states with lifetimes in the μs timescale [3]. Thus, in this system, the stabilisation of radical ions is intrinsic in comparison to natural photosynthesis, where electron transfer cascades cause the spatial separation and stabilisation of the photoexcited radicals. While an instrument-limited upper value of the electron forward transfer time of ≈ 100 fs has been reported [4–6], the early stages of the process are still unexplored. Our recent development of few-optical-cycle laser pulses (5–6 fs) in the visible spectral range by broadband frequency conversion techniques [7] allows now to study extremely fast optically initiated events with unprecedented time resolution. Using this apparatus, we are able to time-resolve for the first time the

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charge transfer process from a polymer chain to a fullerene moiety.

Pump–probe experiments in the fs regime were performed on thin films of conjugated polymers with and without fullerenes. Conjugated polymers are a relatively new and promising class of organic semiconductors with applications in optoelectronics. High efficiency light emitting diodes [8], all organic transistors [9] and solar cells [10,11] have been demonstrated recently. In this work, thin films of poly[2-methoxy, 5-(3′,7′ dimethyl-octyloxy)]-p-phenylene vinylene (MDMO–PPV) [12] and [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) [13], solution cast from 1 wt% solutions of toluene onto thin quartz substrates were studied. The inset in Fig. 1 shows the structural formula of the materials used alongside with a schematic illustration of the photoinduced electron transfer phenomenon. Different samples, with MDMO–PPV/PCBM weight ratios ranging from 1:0.5 to 1:3, were employed. At these high PCBM concentrations diffusion does not influence the dynamics and the intrinsic charge transfer process can be measured. For comparison, pure MDMO–PPV films were also studied. In the highly fullerene loaded composites (MDMO–PPV:PCBM = 1:3 wt. ratio) the luminescence was quenched by three orders of magnitude compared to pristine MDMO–PPV.

Experiments were performed using a visible optical parametric amplifier based on noncollinear phase-matching in β-barium borate, followed by a pulse compressor using chirped dielectric mirrors [7]. This optical source provides ultrabroadband
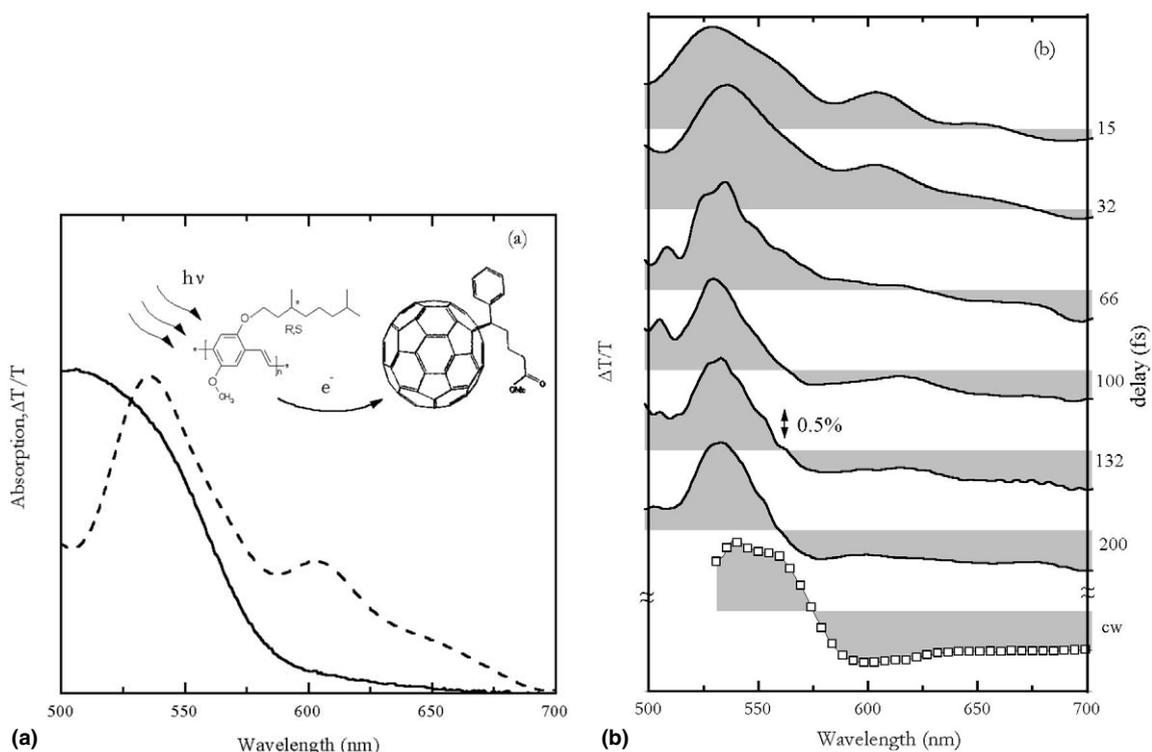

Fig. 1. Spectrally resolved pump–probe spectrum of pristine MDMO–PPV compared to highly fullerene loaded MDMO–PPV/PCBM composites at various delay times. (a) Absorption spectrum of a pure MDMO–PPV film (solid line) and $\Delta T/T$ spectrum at 200 fs pump–probe delay (dashed line). The inset shows a schematic of the photoinduced electron transfer process from MDMO–PPV to PCBM. (b) $\Delta T/T$ spectra of the MDMO–PPV/PCBM blend (1:3 wt. ratio) at various time delays following resonant photoexcitation by a sub-10-fs optical pulse. The cw PA of the blend (□) was measured at 80 K and 10^{-5} mbar. Excitation was provided by the 488 nm line of an Argon ion laser, chopped at 273 Hz.

pulses, with bandwidth extending from 500 to 720 nm, compressed to an almost transform-limited duration of 5–6 fs. The pump–probe setup is based on a standard noncollinear configuration and differential transmission ($\Delta T/T$) is measured using two different techniques: (i) time resolved measurements at a specific wavelength are obtained by spectrally filtering the probe pulse (after passing through the sample) and combining differential detection with lock-in amplification; (ii) $\Delta T/T$ measurements over the entire pulse bandwidth are performed using an optical multichannel analyzer. In all measurements, the maximum signal is a few percent and linearity is verified, to avoid saturation effects. All experiments are carried out at room temperature.

First, the dynamics of pure MDMO–PPV excited by a sub-10-fs pulse is compared with the dynamics of MDMO–PPV/PCBM composites. Fig. 1a shows as a solid line the absorption spectrum of MDMO–PPV and as a dashed line the $\Delta T/T$ spectrum at 200 fs pump–probe delay. In agreement with previous results [14–16], the $\Delta T/T$ signal can be attributed to a superposition of photobleaching (PB) of the ground state absorption and stimulated emission (SE) from the photoexcited state. SE dominates for probe wavelengths longer than 600 nm, for which the ground state absorption is vanishing. The shape of the $\Delta T/T$ spectrum of pure MDMO–PPV does not show any major evolution in the first few picoseconds from photoexcitation, apart from an overall decay. By adding PCBM to the polymer matrix, the excited state evolution scenario changes dramatically. Fig. 1b shows a sequence of $\Delta T/T$ spectra for the MDMO–PPV/PCBM composites excited by a sub-10-fs pulse. At early time delays (see the 15 and 33 fs data) the spectrum closely resembles that of pure MDMO–PPV, confirming the predominant excitation of this molecule. The SE band from MDMO–PPV rapidly gives way to a photoinduced absorption (PA) feature, the formation of which is completed within ∼100 fs. After this initial quick evolution the $\Delta T/T$ spectrum remains stationary on the timescale of the experiment (40 ps). This PA feature is assigned to the PPV cation radical (positive polaron) by comparison to the near steady state

$\Delta T/T$ spectrum of a MDMO–PPV/PCBM composite plotted as hollow squares. This band provides a direct signature for the charge transfer process.

In Fig. 2 the excited state dynamics of pure MDMO–PPV at a probe wavelength of 610 nm is plotted as a full line. The features at negative and near-zero delays at this and other wavelengths are due to coherent coupling and pump-perturbed free induction decay [17]. The rise time of the SE signal was found to be independent from the probe wavelength in a broad wavelength range [560–680 nm] and is assigned to the vibronic relaxation (Kasha's rule). The strong oscillations superimposed on the signal probe the motion of the vibrational wavepacket launched by the ultrashort pump pulse on the multidimensional excited state potential energy surface [18]. Ultrashort pulses
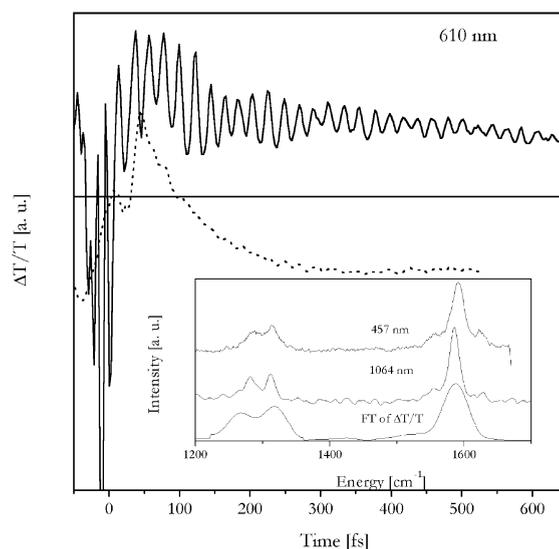

Fig. 2. Quenching of the coherent vibrational oscillations of MDMO–PPV upon the photoinduced charge transfer. The $\Delta T/T$ dynamics for pure MDMO–PPV (——) and of MDMO–PPV/PCBM (1:3 wt. ratio) (- - -), excited by a sub-10-fs pulse, was recorded at the probe wavelength of 610 nm. The inset shows the Fourier transform of the oscillatory component of the MDMO–PPV signal, the nonresonant Raman spectrum of MDMO–PPV (excitation 1064 nm) and the resonant Raman spectrum of a MDMO–PPV/PCBM sample (excitation 457 nm). For the resonant Raman spectrum of MDMO-PPV it was necessary to quench the strong background luminescence by addition of PCBM.

coherently excite vibrational motion both in the ground and excited states of a molecule: in our case, in the SE region, we expect the excited state contribution to be dominant. We performed additional experiments using a chirped excitation pulse [19], which confirmed that the oscillatory component of the signal is composed from a ground state and an excited state contribution, whereas the weights of the two contributions depend on the probe wavelengths. The inset in Fig. 2 shows the Fourier transform of the oscillatory component of the signal as compared to the resonant and nonresonant Raman spectrum of the polymer. The correspondence of the excited state frequencies measured in the pump–probe experiment to the ground state ones measured by cw Raman scattering indicates that no major geometrical rearrangement is taking place following the photoexcitation. This observation supports the now widely accepted assumption that the primary photoexcitations in MDMO–PPV are spatially localized and of molecular (excitonic) character.

The dynamics of the charge transfer process can be determined more accurately by $\Delta T/T$ measurements at a fixed probe wavelength as a function of pump–probe delay. Figs. 2 and 3 show the dynamics of the blend at different probe wavelengths, compared to those of the pure polymer. A fast rise to positive values of $\Delta T/T$, due to SE from the polymer, is followed immediately by a fast decay until the signal stabilises on negative $\Delta T/T$, indicating the PA of the charge transferred state. Probing at around 700 nm, where the polymer shows negligible SE, the $\Delta T/T$ signal goes directly to negative values. These data confirm substantially the results of the spectral measurements (Fig. 1b), proving the rapid formation of the MDMO-PPV charged state, which is completed within ≈ 100 fs after excitation. By an exponential fitting of the PA rise, a time constant for the electron transfer process of 45 ± 3 fs can be calculated.

Experiments performed on blends with MDMO–PPV:PCBM weight ratios ranging from 1:3 to 1:0.5 all displayed the same ultrafast electron transfer process, with a dynamics which was found to be nearly concentration-independent. For much lower PCBM concentrations (weight
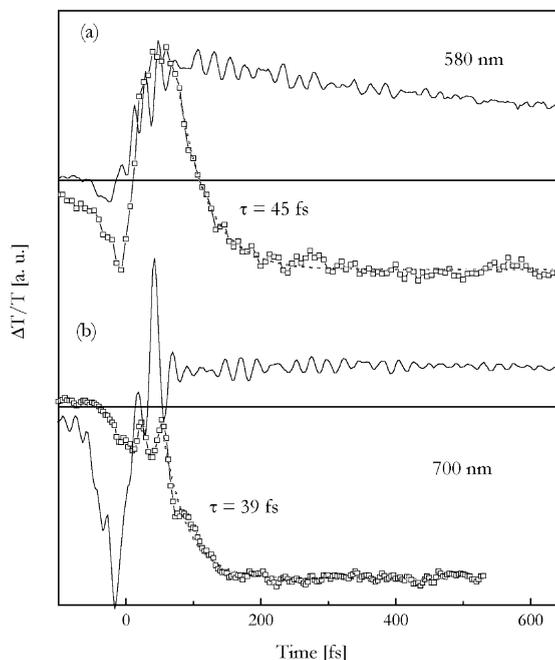

Fig. 3. Time resolution of photoinduced charge transfer in MDMO–PPV/PCBM composites. $\Delta T/T$ dynamics for pure MDMO–PPV (——) and MDMO–PPV/PCBM ($\square$) at the probe wavelengths of 580 and 700 nm. The dotted lines are single exponential fits to the PA of the composites.

ratios lower than 1:0.05), the formation time of the PA band increases to a few ps and the formation rate becomes a linear function of PCBM concentration. This indicates that, as previously observed [20], at low acceptor concentrations we enter a new regime in which the charge transfer process is mediated by disorder-induced diffusion of the excitations, which migrate until they reach a site favourable for charge transfer.

In this work we have demonstrated the potential of a new spectroscopic tool, allowing to perform pump–probe experiments with sub-10-fs time resolution over bandwidths as broad as 200 nm in the visible. Using this source, we were able to directly time-resolve for the first time the ultrafast photoinduced electron transfer from a conjugated polymer to a fullerene. The very fast charge transfer time constant observed ($\tau \approx 45$ fs after Kasha relaxation) implies a large exchange integral of the excited state orbitals of donor and acceptor molecules. Since, however, there were no

new charge transfer bands observed in the linear absorption of the composite, this overlap must involve a resonant interaction of higher lying excited states of the fullerene with the π^* orbitals of the polymer. A detailed theoretical analysis is required to clarify its physical mechanism. In addition, the extreme time resolution allows to directly access, in the time domain, the very fast vibrational motions coupled to the electronic transitions. While coherent oscillations are clearly observed in the pure MDMO–PPV sample, coherence is reduced in the fullerene loaded samples. This result provides additional insight into the physics of the charge-transfer process, strongly suggesting that the system evolves on an anharmonic potential energy surface, which is formed immediately after photoexcitation [21].

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