

Ultrafast charge transfer in conjugated polymer-fullerene composites

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Abstract

Phonon modes, which are strongly coupled to the electronic excitation of the conjugated polymer are coherently excited by sub-10-femtosecond laser pulses. Pump probe experiments show vibrational modulations as fast as 25 fsec. The Fourier transformed spectrum displays the non-resonant Raman spectrum. Addition of fullerenes into the conjugated polymer matrix quenches the vibrational coherence of the polymer due to a strong interaction of the excited polymer with the fullerene moiety. Charge separation times of less than 100 fsec are reported.

Keywords: Time-resolved fast spectroscopy, photoinduced absorption spectroscopy, fullerenes, poly(phenylene vinylene).

1. Introduction

The discovery of charge transfer from conjugated polymers onto fullerenes [1] has initiated a number of new applications, such as photovoltaic plastic solar cells [2]. In this work, the very early time stage of charge separation is investigated using femtosecond pump probe methods. Thin films of poly[2-methoxy, 5-(3',7' – dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV) as well as mixed with [6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM) were studied. Results clearly show the competition of the photoinduced electron transfer even with the coherent vibrational relaxations on the excited polymer giving a timescale of the forward transfer on the order of 50 femtoseconds.

2. Experiment

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. This laser source provides broadband pulses, with bandwidth extending from 500 to 720 nm, compressed to an almost transform-limited duration of sub-10-fs [3]. The pump-probe setup is based on a standard noncollinear configuration and the differential transmission ($\Delta T/T$) is measured. Either time resolved measurements at a specific wavelength are

obtained by spectrally filtering the probe pulse and combining differential detection with lock-in amplification or $\Delta T/T$ measurements over the entire pulse bandwidth are performed using an optical multichannel analyzer.

3. Results and discussion

In Fig. 1 the excited state dynamics of pristine MDMO-PPV at a probe wavelength of 610 nm is presented.

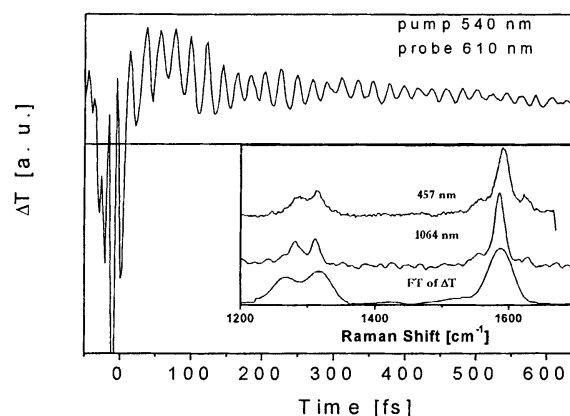


Fig. 1: Femtosecond pump-probe traces of pristine MDMO-PPV. Insert: Fourier transform of ΔT compared to Raman spectra of MDMO-PPV.

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Oscillations due to wave packet motion are clearly observable. The oscillatory features observed at negative and near-zero delay at this and other wavelengths are due to

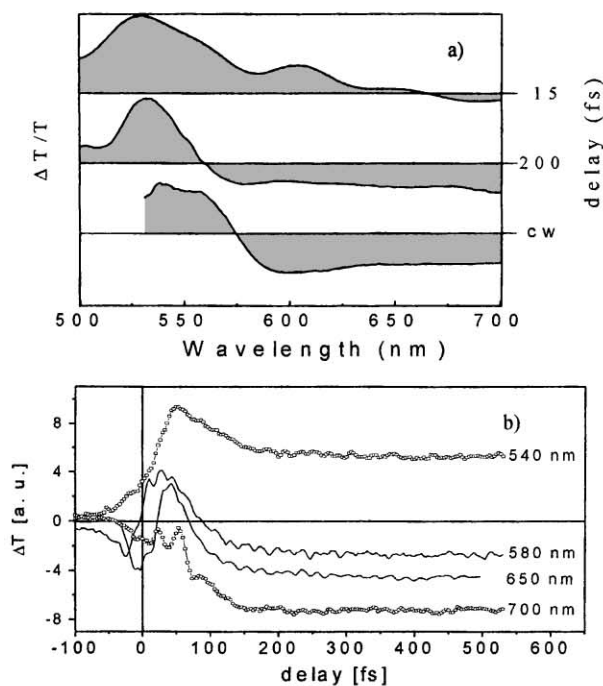


Fig. 2: a) Spectral resolved pump-probe measurements on MDMO-PPV/PCBM composites at 2 delay times and for steady state conditions (cw), b) fs pump-probe traces at various probe wavelength.

coherent coupling [4] and pump-perturbed free induction decay. At positive delay times the ΔT signal underlying the oscillations corresponds to stimulated emission (SE), as the probe wavelength lies at the centre of the luminescence. The rise time of the SE signal was found to be independent from the probe wavelength in a broad wavelength range and is assigned to vibrational relaxation. The 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. Ultrashort pulses coherently excite vibrational motion both in the ground and excited states of a molecule [5]. We performed additional experiments using a chirped excitation pulse, which confirmed that the ground state contribution to the oscillatory component of the signal is small for probe wavelengths longer than 600 nm. The inset in Fig. 2 shows the Fourier transform of the oscillatory component of the signal [6] as compared to the Raman spectra of the polymer. The correspondence of the excited state frequencies measured in the pump-probe experiment to the ground state ones measured by Raman scattering indicates that no major geometrical rearrangement is taking place in the excited state.

Fig. 2a shows a sequence of $\Delta T/T$ spectra for the MDMO-PPV/PCBM composites excited by a sub-10-fs pulse. The $\Delta T/T$ signal at early times can be attributed to a

superposition of bleaching of the ground state absorption (GB) below 570 nm and to stimulated emission (SE) from the excited state for probe wavelengths longer than 600 nm. The SE band from MDMO-PPV rapidly gives way to a photoinduced absorption (PA) feature within 200 fs. After this initial evolution the spectrum remains stationary on the timescale of the experiment (40 ps). The 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 and provides a direct signature for the charge transfer process.

Fig. 2b shows the dynamics of the charge transfer at different probe wavelengths. A fast rise to positive values of ΔT , due to SE or GB of the polymer, is followed immediately by a fast decay until the signal stabilises on negative $\Delta T/T$, indicating the PA of the charge separated state. These data confirm substantially the rapid formation of the MDMO-PPV charged state, which is completed within ≈ 150 fs after excitation. A rise time for the electron transfer process of 45 ± 3 fs can be calculated. Note that the oscillatory features are completely quenched in the MDMO-PPV/PCBM blend, indicating that vibrational coherence is not maintained in the charge-transferred state.

4. Conclusions

Using a sub-10 fsec pulsed laser source, we were able to directly time-resolve for the first time the ultrafast photoinduced electron transfer from a conjugated polymer to a fullerene. A very fast charge transfer time constant of the order of 50 fs after vibrational relaxation was observed. While coherent oscillations are clearly observed in the pure MDMO/PPV sample, vibrational coherence is almost completely lost in the charge-transferred state. This result suggests that the system evolves on an anharmonic potential energy surface, which is formed immediately after photoexcitation.

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