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Direct observation of the ultrafast electron transfer process in a polymer/fullerene blend

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Photoinduced electron transfer in organic molecules is a topic of fundamental interest in photophysics and for applications to artificial photosynthesis. Highly efficient ultrafast electron transfer from photoexcited conjugated polymers to C<sub>60</sub> has been reported [1]; the back transfer is heavily hindered, thus providing a stabilization mechanism of the photogenerated charges. The detailed time resolution of this process is needed to shed light on the charge transfer mechanism.

In this work we perform ultrafast experiments on conjugated polymer/C<sub>60</sub> blends with sub-10-fs time resolution. We are able to time resolve for the first time the charge transfer process, obtaining a time constant  $\tau_{ct} \approx 45$  fs. The excitation source is a visible optical parametric amplifier [2] providing ultrabroadband pulses with sub-10-fs duration and spectrum extending from 520 to 720 nm. We excite thin films of poly [2-methoxy, 5-(3,7-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV), blended with C<sub>60</sub>, with a 1:1 ratio in molecular concentration; at these high C<sub>60</sub> concentrations we measure the intrinsic charge transfer process unaffected by diffusion. For comparison we also study pure MDMO-PPV films.

Fig. 1(a) shows as solid line the differential transmission ( $\Delta T$ ) signal for pure MDMO-PPV at the probe wavelength of 580 nm. The features at negative and near-zero delays are due to coherent artifacts. The  $\Delta T$  signal has positive sign and is assigned to stimulated emission from the excited state. The strong oscillations superimposed on the signal (see Fourier spectrum in Fig. 1b) reflect the vibrational modes coupled to the excited state. By blending with C<sub>60</sub>, the signal changes dramatically (dashed line in Fig. 1(a)). The initially positive  $\Delta T$  rapidly changes sign, indicating the quick formation of a new photoinduced absorption (PA). Based on cw measurements, this new PA is assigned to the MDMO-PPV charged state (polaron) and thus provides a direct signature for the charge transfer process. By an exponential fitting of the PA risetime, a time constant for the electron transfer process of  $\approx 45$  fs is calculated. Similar results are obtained at other probe wavelengths. Excited state vibrational coherence is not maintained in the charge transfer process, thus indicating evolution of the system on an anharmonic charge transfer potential energy surface.

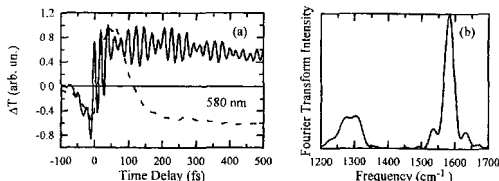


Fig. 1 (a)  $\Delta T$  for pure MDMO-PPV (solid line) and PPV/C<sub>60</sub> (dashed line) at the probe wavelength of 580 nm; (b) Fourier transform of oscillatory component of the MDMO-PPV signal.

References

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12.45 QFG8

Bright and Dark Resonances in Er:YAG: Generation, Measurement and Coherent Control

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Summary

Rare earth ions (RE) with optically activated 4f electrons present sharp spectral transitions in condensed matter due to the shielding of the 4f electrons by the outer 5sp electrons. The "quantum dot" nature of RE makes them ideal for the study of condensed matter structures and dynamics. In this communication, we report on the fluorescence excitation spectra and the coherent femtosecond (fs) dynamics regarding the single ion and pair-transitions in Er:YAG at 77K. We further apply fs interferometric techniques to control the single ion and ion-pair emissions.

The continuous wave Ti:sapphire laser output with the wavelength tunable near the 800 nm spectral region excites the Er from the ground state to an intermediate excited state resulting in linear fluorescence (LF). Previous work demonstrated that the rare earth optical transitions are "inhomogeneously broadened", with pair transition satellites responsible for upconversion normally obscured by a strong linear absorption line [1]. On the other hand, recording of the up-converted signal can separate the pair transitions from a strong linear absorption background.

Fig. 1 shows the fluorescence excitation spectra recorded for LF (upper curve) and for up-conversion (lower curve). The depth and spectral profiles of bright and dark resonances at 786.5, 787.8, 788.5, and 789.0nm are found to be excitation intensity dependent. The bright resonances of upconversion are observed to be a reversed image of the dark resonances in the LF excitation spectra. The excitation cross sections of the two processes can be written as

$$\sigma(\omega, J) + \sigma(\omega, -J) = \sigma(\omega, I=0) \quad (1)$$

where  $\sigma^+$ ,  $\sigma^{NL}$  and  $\sigma^-$  are the absorption cross sections for the LF, upconversion and for LF recorded at very low intensity respectively.

The simultaneously recorded femtosecond interferograms for LF and for up-conversion are shown in the typical time

window 1.0-1.1 ps in Fig. 2. It is obvious that the two interferograms have opposite phase, making coherent control possible to enhance up-conversion while suppressing LF or vice versa.

The physical mechanism responsible for the opposite phase between the two interferograms can be explained with the theoretical analysis of interferograms. An interferogram is related to the absorption cross section by

$$S^i(t_d; \omega) = \int_{-\infty}^{\infty} d\tau \cos(\omega\tau + \phi) I(\tau) e^{i(\omega\tau + \Omega)\tau} \quad (2)$$

Here  $t_d$  is the delay time between the two exciting pulses,  $\Omega$  is the central frequency of the pulses and  $\phi$  is the related phase delay.  $I(\omega)$  is the exciting spectrum and  $\sigma^+$  general absorption cross section for LF or for upconversion. Replacing equation (1) into (2) gives rise to

$$S^i(t_d; \omega) + S^{NL}(t_d; \omega) = S^-(t_d; \omega) \quad (3)$$

As the spectral bandwidth of the excitation spectra for LF is in general much broader than the burned spectral hole width,  $S^+$  goes to zero as a function of  $t_d$  much faster than the terms on the left hand side. As a result,

$$S^i(t_d; \omega) + S^{NL}(t_d; \omega) = 0 \quad \text{for large time delay}$$

suggests the production of the phase shift of  $\pi$  between the two interferograms, making it possible to enhance linear or nonlinear conversion efficiency simply by delaying the excitation pulse pair by the phase delay of  $\pi$ .

References:

- 1 W.M. Yen in "Spectroscopy of solids containing rare earth ions", Ed by A.A. Kaplyanski and R.M. Macfarlane, North Holland, (1987), 185.
- 2. S. Mukamel, "The principles of nonlinear spectroscopy", Oxford University Press, New York (1995)

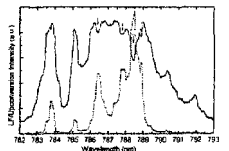


Figure 1. LF (solid line) and upconversion (dotted line) excitation spectra.

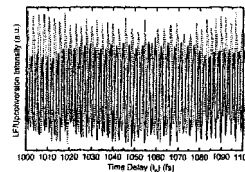


Figure 2. Delay time dependent (solid line) and up-converted signal (dotted line) interferograms in the time window of 1.0-1.1 ps.