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Charge Carrier Generation in a Conjugated Polymer Studied via Ultrafast Pump-Push-Probe Experiments

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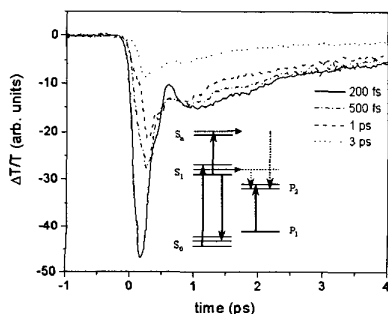
Conjugated polymers find rapidly growing application in electroluminescent displays and are extensively studied for use in photovoltaics and laser diodes. For a wide range of conjugated materials ultrafast pump-probe experiments have revealed the excited state dynamics of singlet and triplet excitons as well as positively and negatively charged polarons. Charge carriers play a key role in all the above mentioned applications. However, there is yet no clear picture of the mechanisms which lead to their generation.

Photo-current excitation cross-correlation measurement, on methyl-substituted ladder-type poly(*para*)phenyl (m-LPPP),¹ a prototypical conjugated polymer with very appealing properties for the above mentioned applications,² have suggested that charge carrier generation occurs preferentially from higher lying states during energy migration.

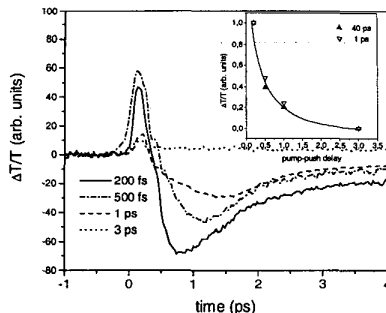
Our approach to examining this mechanism consists of an innovative modification of the ultrafast time-resolved pump-probe technique, namely pump-push-probe (3P). In this technique the S_1 state created by the pump pulse is re-excited by a second pulse ('push') to a higher lying state S_n and a third (probe) pulse measures the sample differential transmission. This method has previously been used³ with push and probe at the same wavelengths, so that only the dynamics of the S_1 - S_n absorption recovery could be observed. The broad band probe employed in the present work allows detection of the spectral signatures of the states created by the push.

3P measurements were performed on drop-cast m-LPPP films using the following combination of 150 fs pulses: pump at 390 nm, push at 780 nm, probe white light continuum.

Fig. 1 shows the 3P dynamics of stimulated emission at 490 nm for different pump-push delays. The negative sign represents the initial re-



QThC5 Fig. 1. 3P dynamics of m-LPPP at 490nm for different pump-push delays. Inset shows scheme of electronic levels of m-LPPP.



QThC5 Fig. 2. 3P dynamics of m-LPPP at 680nm for different pump-push delays.

duction of stimulated emission due to depletion of the S_1 population caused by the push pulse. SE partially recovers on the 200-fs time scale, due to ultrafast internal conversion from S_n , but a significant portion of the S_1 population recombines on a much longer time scale, suggesting the presence of a secondary process initiated by the push pulse.

Fig. 2 displays the 3P dynamics of the photoinduced absorption at 680nm, containing contributions from the singlet exciton and the charge carriers. The initial positive signal is again a signature of the depletion of the S_1 population. Here however the signal changes sign reaching a negative peak after 1 ps following push excitation, pointing out the formation of charged states. Both the magnitude of the absorption at 680 nm and that of the quenching at 490 nm are strongly dependent on the pump-push delays (see also inset of Fig. 3). This proves that the charge generation efficiency be significantly higher in the early stages after photoexcitation, which provides convincing evidence for dissociation of migrating singlet excitons at quenching centers. Experiments with 10-fs time resolution using push and probe pulses from a visible optical parametric amplifier are in progress.

1. C. Zenz, G. Lanzani, G. Cerullo, W. Graupner, G. Leising, S. DeSilvestri, "Dissociation of hot excitons in ladder-type polymer light emitting diodes", submitted to Chem Phys. Lett.
2. G. Hadziioannou and P.F. van Hutten, *Semiconducting Polymers—Chemistry, Physics and Engineering* (Wiley-VCH, 1999).
3. S.V. Frolov, M. Liess, P.A. Lane, W. Gellermann, Z.V. Vardeny, M. Ozaki, and K. Yoshino, "Exciton Dynamics in soluble Poly (p-phenylene-vinylene): Towards an Ultrafast Excitonic Switch", Phys. Rev. Lett. 78, 4285–4288 (1997).

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Dynamic intensity borrowing induced by coherent molecular vibration observed by sub-5-fs spectroscopy

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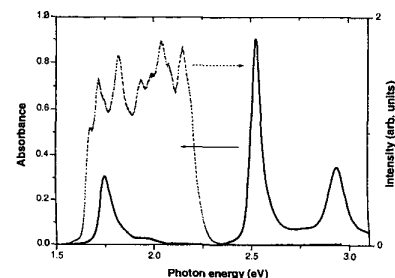
J-aggregates of organic molecules are of great interest because of their ultrafast and large optical nonlinearity induced by the excitonic resonance

and superradiance.¹ Among J-aggregates composed of various aromatic or macrocyclic compounds, tetraphenylporphine tetrasulfonic acid (TPPS) J-aggregates are of special interest since they are model substances for aggregates of the light-harvesting antenna chlorophyll with a storage ring configuration in photosynthesis.² The absorption spectrum of TPPS aggregates (Fig. 1), shows a relatively weak band in the red region and much stronger peaks in the blue-near ultraviolet, denoted as Q- and B-bands, respectively, composing a quasi-two-band Frenkel exciton system. In the present study, we observed for the first time dynamic intensity borrowing which results in the modulation of the Q-transition dipole moment.³

A one-dimensionally oriented film of porphyrin J-aggregates was prepared by the vertical spin coating developed by our group.⁴ The sample was pumped and probed with the sub-5-fs pulses from a nonlinear phase-matched OPA system⁵ at room temperature. The time-resolved induced absorption spectrum is shown in Fig. 2(a). The induced difference absorption spectrum is composed of bleaching and photo-induced absorption (PIA). The bleaching is attributed to the transition between the one-exciton and the ground state, and PIA is associated with the transition to multi-exciton states (MES), because the transition to MES should be observed at higher photon energy side of the Q-band due to Pauli exclusion principle. The induced absorption spectrum is clearly modulated in Fig. 2(a). The modulation frequency is determined to be $235 \pm 15 \text{ cm}^{-1}$ by Fourier analysis (Fig. 2(b)), which is assigned as a 244 cm^{-1} -ruffling mode.⁶ Especially, the Fourier analysis reveals that the phase of the oscillation shows a π -phase difference between the bleaching and PIA. This result indicates that the bleaching and PIA increase (or decrease) synchronously.

The experimental results are well explained by DIB, which gives rise to modulation of Q-transition dipole moment because the oscillator strength is transferred from the B-band to the Q-band. The normalized modulation of the transition dipole moment ($\delta\mu/\mu$) of the Q-transition is estimated from the ratio of the oscillating component to the slow-decay component in the transient signal. Taking account of the modulation of the dipole-dipole interaction, $\delta\mu/\mu$ is estimated as $1.9 \pm 0.1\%$.

In conclusion, coherent molecular vibration coupled to the Frenkel exciton in porphyrin J-aggregates is observed. The oscillation in the transient signal is interpreted by the modulation of the transition dipole moment caused by the DIB



QThC6 Fig. 1. Stationary absorption spectrum of porphyrin J-aggregates (solid) and laser spectrum (dashed).