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## Solvent-controlled acceleration of electron transfer reaction

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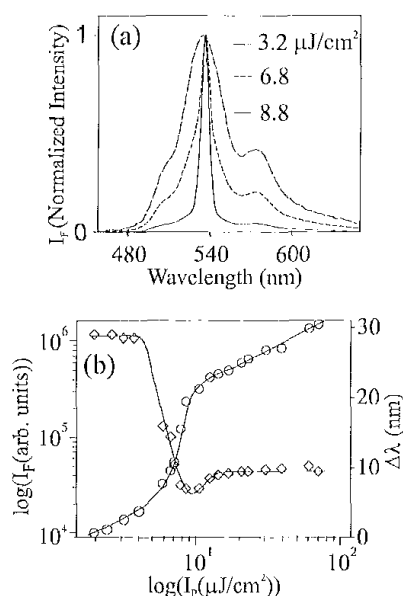
**QFB5**            9:00 am

## Gain dynamics in oriented thin films of an oligo(para phenylene vinylene)

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Numerous factors which govern the efficiency of the stimulated emission process in thin films of electroluminescent conjugated oligomers are related to the structural properties of the materials. Among them the effects of molecular orientation are of major interest.[1,2] It is indeed fundamental to know whether an ordered phase of oligomers is necessary to lower the threshold of the stimulated emission. In this paper we study the role of the molecular orientation by investigating the photo-excited states dynamics of crystalline thin films of the 5-ring n-octyloxy-substituted oligo(p-phenylene vinylene) (Ooct-OPV5) with femtosecond pump-probe spectroscopy. In particular we compare the emission properties and gain dynamics of two categories of crystalline films characterized by different degrees of structural disorder.

Our observations are in favor of the fact that slight variations of the molecular organization can have a considerable impact on the gain mechanisms. For instance the amplification of spontaneous emission is shown to occur under drastically different conditions depending on the crystalline quality of the film, the lowest threshold for ASE being reported in the most
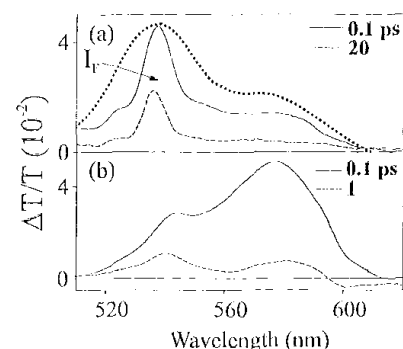


highly ordered films provided that the pump is polarized parallel to the chain axis (Figure 1). Under similar conditions of excitations a quenching effect occurs when the degree of disorder in the film increases. This quenching can be explained considering the evolution of the gain in both time resolved (Figure 2) and spectrally resolved experiments. In the less ordered samples we are able to make the link between the strong depletion of the gain observed at high pump fluences and the appearance of a photo-induced absorption band which we attribute to the opening of new dissipative channels induced by the disorder, such as transitions to higher electronic states.

In addition, the very high crystal quality of the thinnest films (100 nm) allows us to point out other fundamental aspects concerning limitation factors inherent in the vibronic structure of the molecule. We show that depending on the regime of amplification, modifications occur in the spectral shape of the dynamical gain (Figure 3). For high pump fluences the gain is favored on the lowest vibronic transition (580 nm) at the expense of the main peak (535 nm). Such behavior of the gain band observed in highly ordered films reflects a complex dynamics of the populations in the ground and excited states of the oligomer. It must nevertheless be considered as an additional intrinsic source of limitation in regard to the development of materials with optimized

**QFB5**    **Fig. 1.** (a) Evolution of the time integrated luminescence spectra in the Ooct-OPV5 well ordered 100 nm thick films with absorbed pump energy density $I_p$ (the pump is polarized parallel to the chains). (b) Details of the corresponding intensity (circles) and line width (diamonds) as a function of $I_p$. Threshold for ASE is about 6 μJ/cm². It is four times higher in thicker films, which are less ordered, and for which the ASE is obtained for an excitation polarized perpendicular to the chain axis.
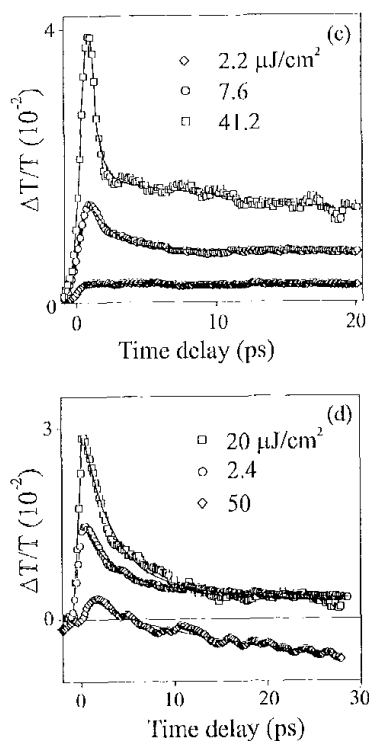


**QFB5**    **Fig. 2.** Time resolved differential transmission (at λ = 535 nm) of Ooct-OPV5 for increasing absorbed pump energy densities: (a) in the 100 nm thick film, (b) in the 200 nm thick film. The polarization of the pump is parallel to the chain axis. Above about 12 μJ/cm² a competition between gain and induced absorption occurs leading to quenching in the thicker film.



**QFB5**    **Fig. 3.** Differential transmission spectra of the Ooct-OPV5 thin film for two absorbed pump energy densities of 10 (a) and 50 μJ/cm² (b) at different delays (solid and dashed lines). (a) The dynamic gain spectra is narrowed in the regime of amplification in comparison to the non stimulated gain which reproduces the spectra of spontaneous emission (dotted line). The corresponding time integrated fluorescence spectra in the regime of ASE (shaded curve) is shown for reference. (b) For high pump fluence and at short delays the signal on the lowest vibronic transition (580 nm) is enhanced at the expense of the main gain peak (535 nm).

structural properties in view of their application to opto-electronic devices.

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**QFB6**            9:15 am

## Solvent-controlled acceleration of electron transfer reaction

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Liquid phase electron transfer is one of the key reactions in nature and has been extensively studied.[1,2] In his pioneering work, Marcus modelled electron transfer (ET) as thermally activated barrier hopping.[1] Subsequent improvements of the theory that incorporated the influence of solvent dynamics on the ET process, led to the central conclusion that inverse ET rate is linearly proportional to the longitudinal relaxation time of the solvent.[3]

In this Contribution we present the first—to the best of our knowledge - experimental evidence of the solvent-controlled rate of the intermolecular ET reaction. The key virtue of the study is the use of binary mixtures, which allows us to vary continuously the relaxation properties of the solvent. We demonstrate that the ET reaction rate can be increased by more than a factor of 5,
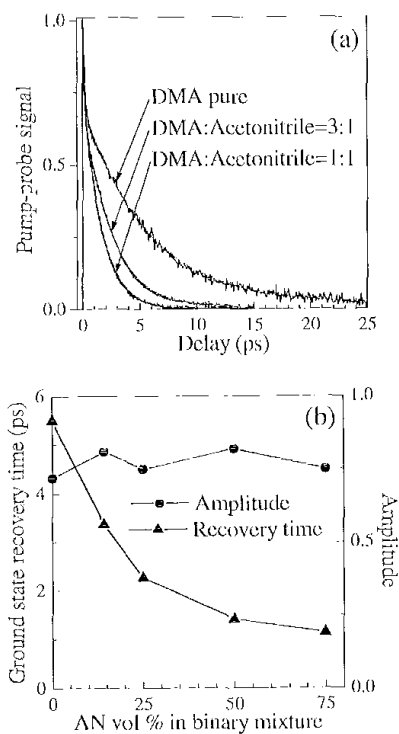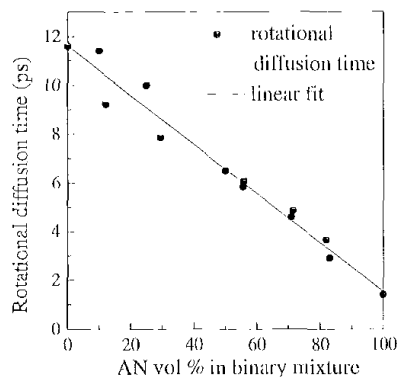
**QFB6** Fig. 1. Pump-probe transients (a) and the ground-state recovery time and amplitude as functions of AN concentration (b). In (a), biexponential fits to the experimental data are shown by thin lines.



**QFB6** Fig. 2. The rotational diffusion time in binary mixtures obtained from the OHD-Kerr experiment. The linear fit to the data is shown by the solid line.



**QFB6** Fig. 3. The backward ET time as a function of longitudinal relaxation time. The fit to the experimental data (solid circles) is shown by the solid line.

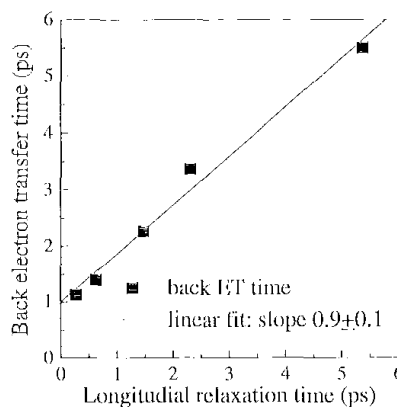which signifies the change from solvent-controlled ET to a non-adiabatic ET.

As a model system for the study of the influence of the solvent-dynamical properties on inter-molecular ET, a photo-acceptor dye Rhodamine 800 (R800) molecule in N,N-dimethylaniline (DMA) electron donating solvent is used. It has been shown for similar systems[4] that upon the optical excitation of the dye molecule ET occurs from solvent to the dye. We choose acetonitrile (AN) as the second solvent in the binary mixture since it is one of the fastest responding solvents.

Pump-probe transients obtained for R800 dissolved in DMA/AN mixtures, show a bimodal behavior (Fig. 1a). The initial 150-fs component is caused by the depletion of the excited state population through the forward ET. A longer, ~5.5-ps component, is assigned to the ground-state recovery during backward ET from R800 to DMA. This component demonstrates a remarkable sensitivity to the AN content: the decay time rapidly decreases down to 1 ps with the increase of AN concentration. The pump-probe signal obtained for R800 in pure AN does not exhibit any substantial decay in the experimental time window which is consistent with the absence of the ET process. Figure 1b summarizes the obtained results on the backward ET time. Note that the amplitude of the slow component remains constant in all cases, which indicates that the quantum yield of ET does not decline as the AN concentration increases.

To determine the longitudinal relaxation, we measure the Debye relaxation time by using

the OHD Kerr technique[5] and scale it by the $n^2/\varepsilon$ ratio with $n$ and $\varepsilon$ being the index of refraction and the static dielectric constant, respectively.[6] The relaxation times of binary mixtures show a linear dependence on the AN concentration (Fig. 2). This is fully consistent with the fact that the rotational relaxation time depends on the bulk parameters of the solvent (i.e., viscosity and density) which vary almost linearly with the concentration of either component.

In Fig. 3 the backward ET time is plotted against the solvent longitudinal relaxation time. A linear dependence predicted by theoretical models[3] is clearly observed. Furthermore, the slope of the linear fit to the experimental points amounts to 0.9 ± 0.1, which coincides with the upper limit of 1 predicted for the case of the barrierless solvent-controlled ET. Extrapolation of the straight line in Fig. 3 to zero shows that the backward ET time in an infinitely fast solvent would be ~1 ps. Therefore, our data convincingly demonstrate that the solvent relaxation is the predominant rate-limiting process for the intermolecular ET reaction in pure DMA. However, with the increase of the AN concentration the rate becomes mainly determined by

the electronic coupling between donor and acceptor.

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**QFB7** 9:30 am

## Ultrafast photoelectron spectroscopy of dye-doped organic films

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The electroluminescent organic material, tris(8-hydroxyquinoline)aluminum (Alq), is foremost in organic light emitting device (OLED) fabrication.[1] Doping Alq with highly fluorescent dyes enhances the emission, and allows color tuning.[2,3] Furthermore, DCM doped Alq films have been shown to lase at low photoexcitation thresholds, and have the potential for electrical pumping.[4,5] These applications benefit from detailed understanding of the Alq-DCM excitation transfer, the recombination dynamics, and the energy gap values. Each of these properties were studied in this work.

A Ti:sapphire laser, producing 90 fs, 790 nm, 1 mJ pulses at 500 Hz was used for these experiments. The excitation beam is frequency doubled to 395 nm, the peak of the Alq absorption. The probe beam, which is the 17th harmonic of the laser at 26.7 eV, is generated by high-harmonic conversion. The photoemitted electrons are energy analyzed using time-of-flight spectroscopy.[6,7]

Fig. 1 shows a zero-delay photo-excited electron spectrum of Alq doped with 2% DCM. The lowest unoccupied molecular orbital (LUMO) region is expanded, and an unexcited lowest unoccupied molecular orbital (LUMO) is included for comparison. The zero-delay, occupied-to-unoccupied energy gap is ~2.95 eV. Fig. 2 shows that this gap shrinks on a 10 ps timescale.

The dynamics follow a five-step process: 1) an Alq electron is photoexcited to the LUMO, 2) this electron relaxes within the excited state, 3) the excitation transfers from Alq to DCM, 4)