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Photoinduced Absorption Studies of the Deactivation of Excited Electronic States in Highly Ordered Films of Oligothiophenes

TMR Large-Scale Facilities Access Programme

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Photoinduced Absorption Studies of the Deactivation of Excited Electronic States in Highly Ordered Films of Oligothiophenes

**An experiment performed with funding from the
TMR Large-Scale Facilities Access Programme**

**Access to Lasers at the Central Laser Facility Rutherford Appleton
Laboratory Contract No. ERBFMGECT950053**

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SUMMARY

This report describes the experiment entitled 'Photoinduced absorption studies of the deactivation of excited electronic states in highly ordered films of oligothiophenes'; carried out at the Central Laser Facility (CLF) from the 15th February to the 5th March 1998. The experiment, funded by the Framework IV Large-Scale Facilities Access Scheme, was proposed by Dr D Oelkrug, Institute for Physical Chemistry, Germany and carried out by visiting researchers from the Institute. They were supported by researchers from the Central Laser Facility, Rutherford Appleton Laboratory.

Results Summary

- The de-activation of excited electronic states in highly ordered films was studied using transient absorption technique aiming at explaining unusually low fluorescence quantum yields observed within these systems.
- The results indicate that initially formed excited singlet states undergo a second order S_1 - S_1 annihilation process as well as de-activation through long lived triplet states.
- These results enhance our understanding of a class of compounds important for future electroluminescent devices and field effect transistors.

Arising Publications

Conference presentations

D. Oelkrug, H.-J. Egelhaaf, J. Gierschner, B. Lehr, L. Lüer, G. Lanzani, P. Matousek, "Excited-State Reactions in Vapor Deposited Films of Polyconjugated Organic Molecules" IUPAC Photochemistry Conference, Barcelona/Spain, 1998.

D. Oelkrug, H.-J. Egelhaaf, J. Gierschner, B. Lehr, L. Lüer, G. Lanzani, P. Matousek, "Excited-State Deactivation in Vapor Deposited Films and Nanoparticles of Oligothiénylenes and Oligophenylenevinylens" Europhysics Conference, Varenna/Italy, 1998.

D. Oelkrug, H.-J. Egelhaaf, J. Gierschner, B. Lehr, L. Lüer, G. Lanzani, P. Matousek, "Photogeneration and Decay of Charged Species in Conjugated Organic Films - A combined Femtosecond Absorption, Luminescence and Conductivity Study", Bunsen International Discussion Meeting, Heidelberg/Germany, 1998.

* the corresponding full paper is to appear in "Physical Chemistry - Chemical Physics", Spring 1999.

Internal Reports

D. Oelkrug, H.-J. Egelhaaf, B. Lehr, J. Gierschner, L. Luer, P. Matousek, M. Towrie. "Photoinduced Absorption in Thin Oligo(phenylenevinylene) Films", RAL Annual Report 1997/98.

The CLF makes beam time at its facilities available to European Researchers with funding from DG-XII, CEC under the Large-Scale Facilities Access Scheme. For further information contact Dr. Chris Edwards at the CLF. Tel: (0)1235 445582, e-mail: c.b.edwards@rl.ac.uk



From left to Right:

Dr. B Lehr, Dr. H-J Egelhaaf and Prof. D Oelkrug

Photoinduced Absorption Studies of the Deactivation of Excited Electronic States in Highly Ordered Films of Oligothiophenes

INTRODUCTION

Derivatives of poly(phenylenevinylene)s (PPV) and polythiophenes (PT) are widely investigated as active components in organic electroluminescent devices and field effect transistors^{1, 2}. The basic physicochemical processes of creation and recombination of charged intermediates can be investigated with fast spectroscopic techniques³⁻⁵.

In this report we describe optical pump-probe experiments on thin films of vapour-deposited oligo(phenylenevinylene)s nPV with $n = 2$ and 3 vinylene units.

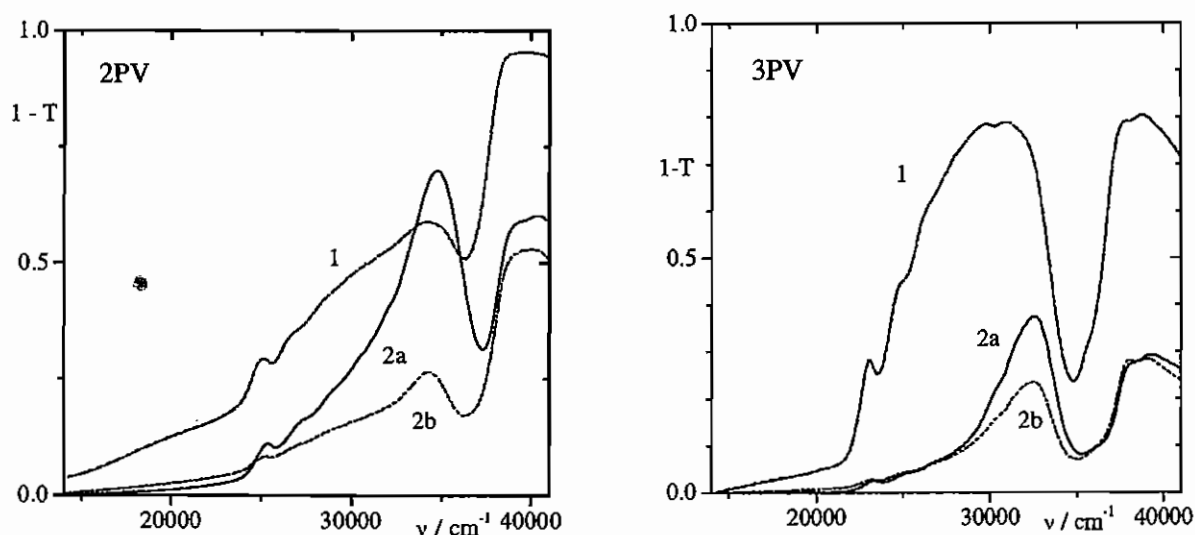


Figure 1 Ground state absorption spectra of 2PV (film thicknesses $d = 90$ nm (1), $d = 55$ nm (2)) and 3PV films ($d = 70$ nm (1), $d = 10$ nm (2)) on fused silica. Light p-polarized, incident under $\alpha = 0^\circ$ (1, 2b) and $\alpha = 60^\circ$ (2a).

Figure 1 presents the ground state absorption spectra of 2PV and 3PV films on fused silica substrates. The 2PV molecules are highly oriented with their long axes perpendicular to the substrate plane, resulting in strongly anisotropic absorption spectra. The 3PV molecules still show short range intermolecular side-by-side arrangement, but no macroscopic preference with respect to the substrate plane. The spectral position of the main absorption region of 3PV fits very well with the 2nd harmonic of the CLRC femtosecond pump-probe-laser equipment,

whereas 2PV absorbs at shorter wavelengths and can be excited only in the weakly absorbing red-edge region. Thus, we concentrate on the results obtained with 3PV films.

MATERIAL AND METHODS

The samples were prepared by vapor deposition of nPVs under high vacuum onto planar fused silica substrates at film thicknesses of $d = 10 - 90$ nm.

The OPA system in the Lasers for Science Facility Ultrafast Spectroscopy Laboratory was used at a repetition rate of 40 KHz and provided both pump (ca. $0.02 - 5$ mJ.cm⁻² at $\lambda = 390$ nm) and probe (ca. $0.005 - 0.75$ mJ.cm⁻²) pulses (ca. 600 fs instrument response function). The beams were overlapped at the position of the thin film sample. The pump beam was chopped at ca. 2 kHz, and the probe beam was sampled by two photodiodes, detecting both sample and reference signals. The data were collected, by lock-in amplifier, as kinetic traces at single probe wavelengths, selected by use of interference filters.

RESULTS

Two regions with intense transient absorption signals could be distinguished in the wavelength regions of 800 – 1000 nm (region 1) and 550 – 650 nm (region 2). In addition we investigated region 3 at 440 – 500 nm where ground state depletion and stimulated emission can be expected.

The very intense absorption signals, up to $DT/T = 0.3$, obtained in region 1 are assigned to excitonic singlet-singlet absorption ($s_1 \rightarrow s_n$), since a very similar signal can be observed also in dilute 3PV solutions in CH₂Cl₂. The rise and decay kinetics of the $s_1 \rightarrow s_n$ absorption have been monitored at $\lambda = 900$ nm. The main results are presented in Figure. 2. The normalised decay traces show clearly that the decay kinetics are strongly dependent on the pulse intensity. The decay traces are shorter than in dilute solution by more than one order of magnitude. The excitonic decay in solution is exponential with $\tau \approx 920$ ps, which is identical to the fluorescence decay time. Contrary to region 1, the signal decay curves of region 2 are independent of the laser intensity (Figure. 3). The rise times are very fast (within the pump pulse width), but the decay is very nonexponential, extending from $\tau_{\text{init}} \approx 100$ ps to $\tau_{\text{fin}} > 10$ ns.

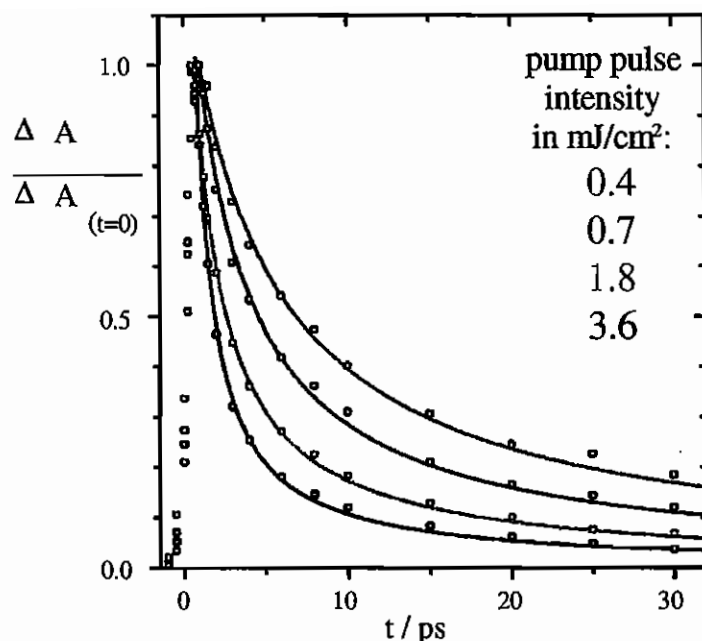


Figure 2. Normalized decay traces of the $s_1 \rightarrow s_n$ absorption of a 3PV film ($d = 70$ nm) on fused silica at different pump pulse intensities (observed at $\lambda = 900$ nm).

KINETIC ANALYSIS

All $S_1 - S_n$ decay curves in Figure. 2 can be analysed with conventional second order kinetics

$-\frac{dS_1}{dt} = k_{ss}S_1^2$ inserting a single decay constant of $k_{ss} = (2.8 \pm 0.3) \cdot 10^{12} \text{M}^{-1}\text{s}^{-1}$. Thus, the main part of excited singlets annihilate bimolecularly according to $2S_1 \rightarrow S_n + S_0 \rightarrow S_1 + S_0$. Figure. 4 proves this mechanism since the kinetics of ground state recovery is identical with the S_1 decay trace.

The rise and decay of Figure 3 is tentatively assigned to the formation and decay of radical ions $S_1 + S_0 \rightarrow D^{*+} + D^{*-}$. The formation rate is much faster than the decay rate of S_1 so that it is reasonable to assume that the radical ions can be formed with high yield only from the vibronic S_1 states. The initial fast decay of the radical ions is assigned to geminate recombination since the kinetics is independent of the laser intensity (the long lived radical ions cannot be analysed with the pump-probe technique).

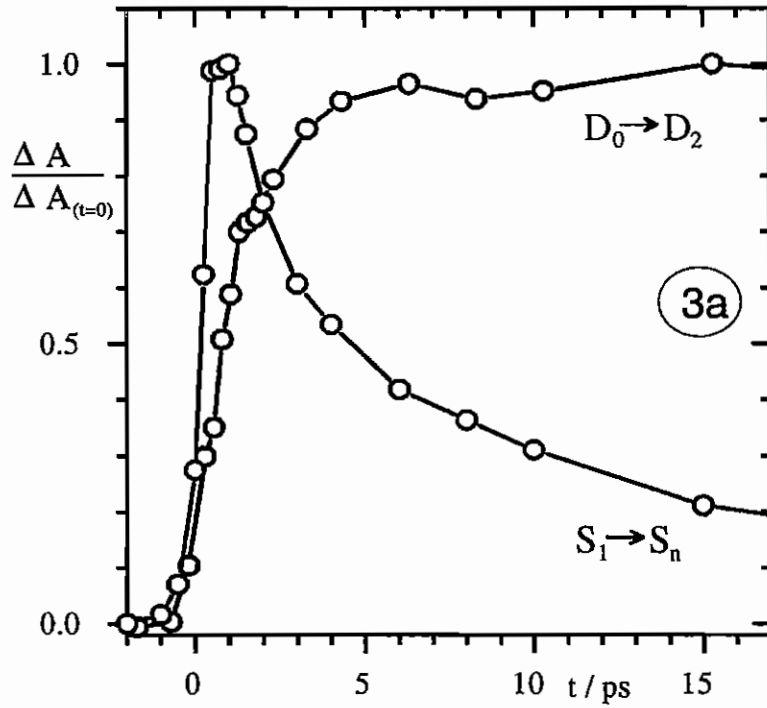


Figure 3. a) Normalized rise curve of the transient absorption of a 3PV film ($d = 70 \text{ nm}$) observed at $\lambda = 620 \text{ nm}$ (assigned to the $D_0 \rightarrow D_2$ transition in 3PV radical ions) and normalized decay trace of the $s_1 \rightarrow s_n$ absorption,

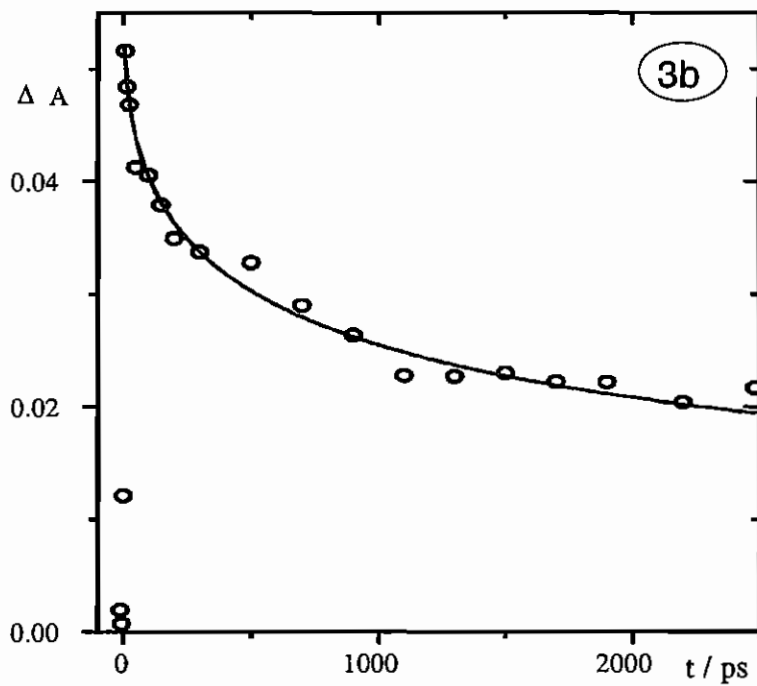


Figure 3. b) decay of the $D_0 \rightarrow D_2$ absorption.

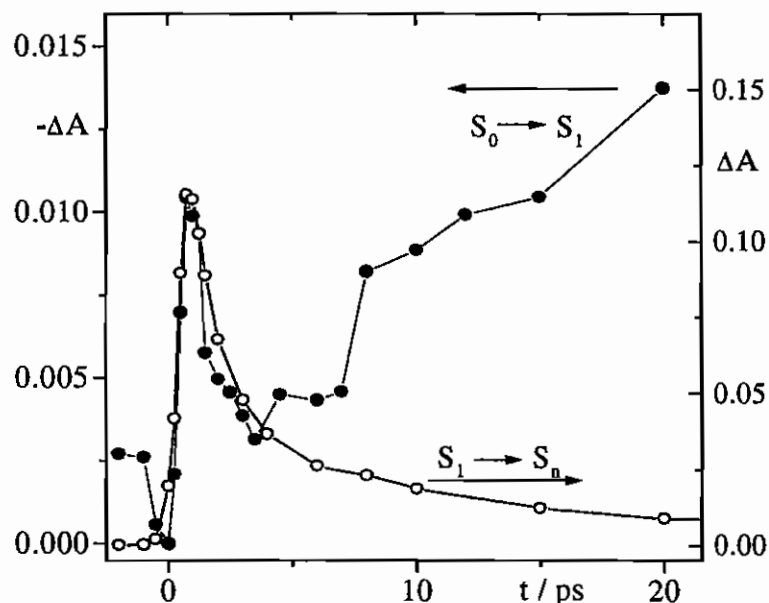


Figure 4. Ground state bleaching and recovery ($s_0 \rightarrow s_1$) of a 3PV film ($d = 70$ nm) observed at $\lambda = 460$ nm, and decay trace of the $s_1 \rightarrow s_n$ absorption.

CONCLUSIONS

The present studies have shown the potential of the pump-probe technique in the elucidation of ultrafast processes in organic thin films. Further work is needed to conclusively assign the observed decay traces to transient species. This will be greatly assisted by spectral detection, e.g. by an optical multichannel analyzing (OMA) system. In order to reduce thermal effects, measurements have to be performed at lower light levels (requiring enhanced signal to noise ratio) and smaller beam spot areas. In order to investigate the effects of oxygen and of temperature on the photophysics of organic films, especially on charge carrier formation and recombination, experiments under high vacuum and at cryogenic temperatures are necessary.

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