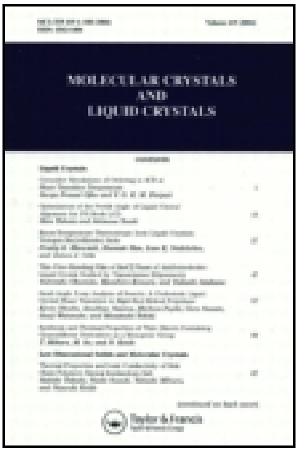

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Ultrafast Fluorescence Spectroscopy of PPV

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ULTRAFAST FLUORESCENCE SPECTROSCOPY OF PPV

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Abstract The spectrally resolved decay of photoluminescence in PPV - type conjugated polymers has been measured employing fluorescence-up-conversion and Streak-camera techniques. The results are in account with the concept of stochastic excitation transport amoung an energetically disordered manifold of chromophores, identified as subunits of the polymer chain comprising several repeat units. They demonstrate that the primary excitations are of excitonic origin.

INTRODUCTION

The nature of optically generated elementary excitations in conjugated polymers as well as their dynamics is currently under debate. The conventional notion has been that these systems behave like 1-D semiconductors tractable in terms of the SSH Hamiltonian [1] that ignores Coulomb as well as electron correlation effects but invokes strong electron phonon interaction. Disorder as well as interchain effects are considered to be of secondary importance. The elementary optical excitations are believed to be free electron -hole pairs, generated with unit quantum efficiency , that rapidly self-localize to form polarons and bipolarons. The former can recombine radiatively giving rise to photoluminescence associated with a Stokes shift that reflects the polaron binding energy. Photoconduction action spectra [2,3] as well as photo-induced absorption[4] support this concept.

The alternative model is based upon a molecular approach. Given the fact that the chains in a non-crystalline polymer are not perfectly aligned it appears straightforward to treat a conjugated polymer as an array of subunits whose length, the effective conjugation length L_{eff}, depends on sample perfection and is, concomitantly, subject to statistical variation. The absorption spectrum reflects the inhomogenously broadened vibronic $S_1 \leftarrow S_0$ absorption manifold of these subunits, their elementary excitations being coulombically bound electron-hole pairs, no different from the elementary excitations of oligomeric model compounds [5]. The fact that the absorption spectra of partially ordered conjugated polymers, such as stretch-aligned PPV, reveal vibronic fine structure and differ from those of their corresponding oligomers only by some red-shift is in accord with this notion [6]. Further support comes from the recent observation that site selectively excited luminescence spectra of both π and σ-conjugated polymers reveal little if no Stokes shift indicating that electron-phonon interaction is weak and comparable to that of oligomers [7,8]. Recent theory, moreover, proves that electron-hole interaction has to be taken into account for an adequate description of the linear and non-linear optical properties [9,10].

The present paper draws upon time dependent aspects of photoluminescence in PPV-type systems in order to distinguish between both conceptional approaches by probing the temporal decay of PL of PPV-type systems at different spectral positions overlapping with the absorption spectrum employing up-conversion and streak camera techniques. The results are analysed in terms of a computational framework [11] based upon the stochastic hopping motion of excitations within an energetically random manifold of localised states identified with subunits of the polymer chain.[12,13]

EXPERIMENTAL AND RESULTS

Time resolved PL experiments were performed with films of poly-phenylenevinylene (PPV) poly-phenyl-phenylenevinylene (PPPV) and a 1% blend of PPPV in polycarbonate (PPPV/PC). PL was excited by either 150 fs pulses of a frequency doubled Ti-saphire laser (hv = 3.12 eV) or 7 ps pulses of a synchronously pumped coumarin 102 dye laser (2.66 eV). The temporal decay of the spectrally resolved PL was detected employing either the fluorescence up-conversion technique (time resolution 300 fs) or the Streak camera technique (time resolution 20 ps). The spectral resolution of the monochromator was < 20 meV. Experiments on PPV reported already [14], were done at 295 K, those on PPPV and PPPV/PC at 10...13 K.

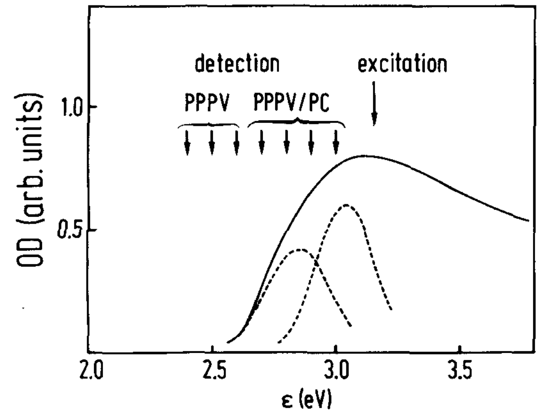

Fig. 1
Absorption spectra of PPPV film and PPPV/PC blend

Fig. 1 shows the absorption spectrum of PPPV including the spectral positions at which PL was monitored. The same spectrum is observed for PPPV/PC indicating that the chain morphology is unaffected by blending. The spectrum does not reveal any vibronic splitting and the indicated convolution into an inhomogeneously broadened $S_1 \leftarrow S_2$ 0-0 transition and a vibronic satellite is only justified by a comparison with PPV and with the vibronic respectively structure of PL spectra. It has been pointed out before [8] that the lack of vibronic splitting is a reflection of the larger disorder the bulky substituent generates in PPPV as compared to PPV. As a consequence the effective conjugation length L_{eff} is shorter than in PPV (≃ 6.....7 repeat units) and statistical variations translate into a larger spread of the transition energies. A crude deconvolution procedure locates the center of the $S_1 \leftarrow S_2$ 0-0 band at 2.83 eV and yields a Gaussian width $\sigma = 0.13$ eV as compared to 2.50 eV and 0.08 eV, respectively, in PPV. Since PL spectra for PPV have already been published [14] only the time resolved PL of PPPV/PC and PPPV shall be reported

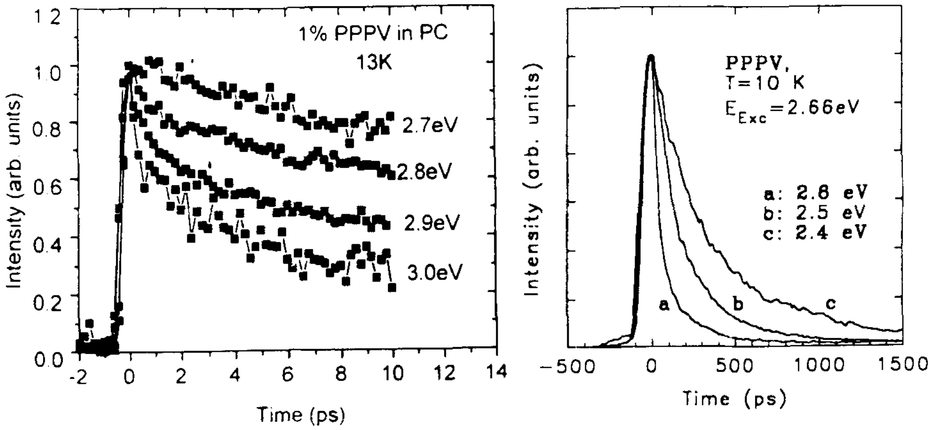

Fig. 2 Spectrally resolved luminescence decay measurements. Left portion: up-conversion date, right portion: Streak camera data

herein. Fig. 2 demonstrates that i) PL occurs within a spectral range that overlaps with absorption , (ii) there is a fast initial rise of PL determined by the width of the larger pulse and the time resolution of the circuit except when detection occurs at the tail of the absorption band, (iii) the time scale of PL decay increases drastically as the spectral detection windows is scanned towards lower energies, and (iv) the decay of PL is non-exponential except at lowest detection energies at which the luminescence lifetime is close to that of an oligomeric model compound (1.5 ns) [15]

DISCUSSION

The observation that PPV-type conjugated polymers show PL on a 0.1 to 10 ps time scale within a photon energy range that overlaps with a absorption is at variance with the one electron semiconductor picture. To analyze the experimental results we shall therefore pursue the concept of excitation migration in energetically random systems and check its applicability.

The method applied to mimic dispersive excitation transfer consists of a Monte Carlo - master equation hybrid technique that generates chain configurations and

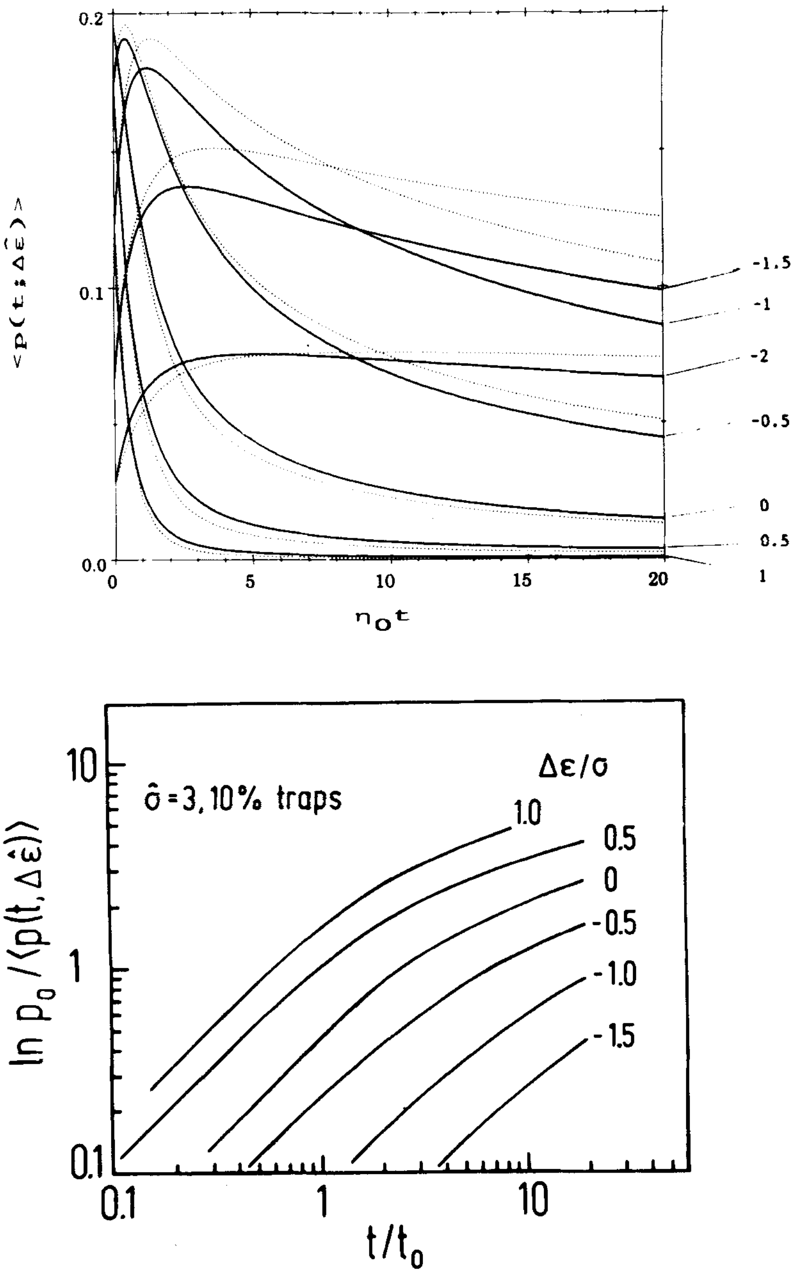

Fig. 3 Computed survival probability of excitations started randomly within a Gaussian DOS of normalized width $\sigma/kT=3$ containing 10% deep traps. The parameter indicates the energetic position of the detection window relative to the center of the DOS in units of σ. Data are shown in linear (top) and logarithmic KWW-type representation (bottom)

solves the incoherent excitation hopping problem by calculating the relaxation profile of the energy-dependent survival probability which is directly related to the spectrally resolved PL response. The chain is a simple hard-sphere model synthesized by a self-avoiding random walk on a cubic lattice. Typically, the chain carries 50 sites located at the intersections of the bond vectors that mimic the typical sequence of arylene-vinylene-repeat units in PPPV. Chains consisting of i) pure donors and ii) donors and traps randomly attached to the chain have been investigated. The dispersion of donor site-energies, i.e. the statistical fluctuation of conjugation lengths has been modelled in terms of a Gaussian distribution of states (DOS) with standard deviation σ. Traps have been assumed to lie energetically below the Gaussian DOS.

The transition rate for jumps of an excitation from site i to j have been assumed to be of the Förster type multiplied by a Boltzmann factor in the case of energetic upward jumps. Since in experiment population of the zero vibronic S_1 levels of the chromophores occurs via rapid ($\simeq$ 100 fs) relaxation form vibrationally excited S_1 states [14] that erodes any site-selectivity the computations of excitation dynamics are performed on the premise of random initial site populations. The computed quantity is the survival probability of an excitation within an energy slice of width $\sigma/2$ centered at selected energies within the DOS.

Fig 3 shows a family of decay curves for the survival probability $<p(t,\Delta\varepsilon)>$ in a system containing 10% of traps in both linear and $\lg\ln p_0/p$ vs. lgt representation, respectively. The latter should yield a straight line with slope provided that $<p(t)>$ is a stretched exponential with exponent $0< \beta < 1$. The time scale is normalized to the nearest neighbor transfer time t_0 in a system composed of isoenergetic chromophores. Fig 3b confirms the intuitive notion that because of the regular structure of the test system the initial decay of the survival probability is exponential and approaches asymptotically a KKW behavior charactersitic of energy transfer in spatially random systems. Lowering the detection energy shifts the decay pattern towards longer times. On the other hand, increasing the relative amount of energetic disorder from $\sigma/kT = 3$ to $\sigma/kT = 20$ has little effect because in the early time domain excitation dynamics is controlled by energetic downhill jumps.

Replotting the experimental data of Fig 2 on a $\lg\ln I_0/I(t)$ vs lgt time scale (fig 4) reveals overall agreement with the computations the only difference being that in experiment turn-over to KKW behavior occurs earlier. This is to be expected since PPPV present as bulk film or as blend should feature a distribution of transfer

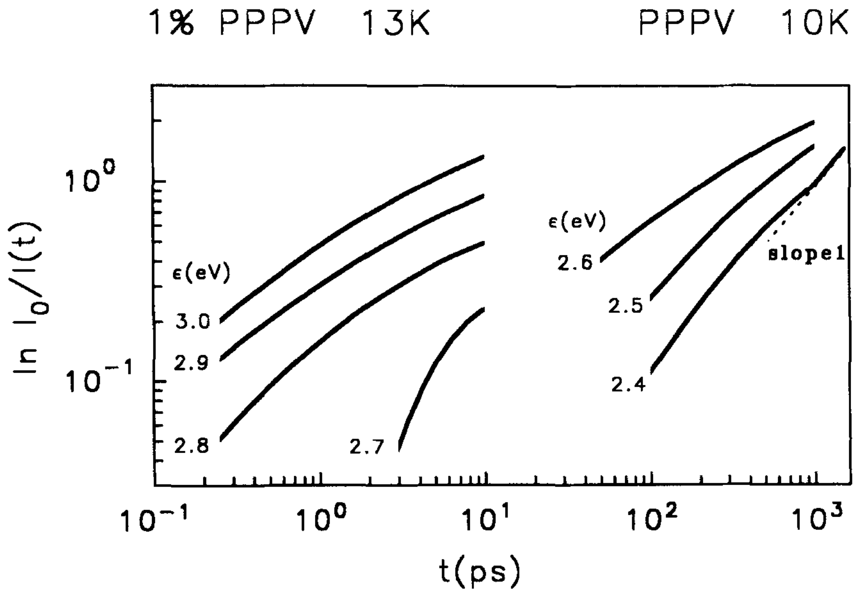

Fig. 4 Experimental data of fig 2 in KWW representation

distances not contained in the model system. The asymptotic β-value is 0.4 consistent with the result of the computations. The absolute time scale of the experiment combined with an assumed nearest neighbor transfer distance of 6 Å and an intrinsic lifetime of the S_1 state of a chromophore yields a Förster radius $R_0 = 18$ Å which is a realistic value for donor-donor transfer.

It should be mentioned that successful data filling requires presence of traps. Their existence has been proven by independence spectrally integrated PL decay measurements [17]. An evaluation of the trap concentration would require calibration with a known amount of quenchers, though, because an excitation delocalised within a chromophore of length L_{eff} will be able to sample several trapping sites and the Förster radius for donor/trap transfer is likely to be > 18 Å.

In summary the present results demonstrate that the concept of stochastic excitation transport among an energetically dispersed manifold of hopping sites is both able and necessary to rationalise time resolved PL measurements in PPV-type conjugated polymers. This implies that the primary excited state is of excitonic nature. Photoconductivity measurements are not inconsistent with this notion since the presence of disorder facilitates exciton dissociation into geminate e...h pairs [18]

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