Site-selective spectroscopy of matrix-isolated conjugated polymers

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Abstract. Fluorescence spectra of poly(phenylphenylenevinylene) (PPPV) and poly(diphenylenediphenylvinylene) (PDPV) incorporated in a glassy methyltetra-hydrofuran matrix have been measured at 6 K upon site-selective excitation. Their shift with excitation energy above what is commonly referred to as band gap is incompatible with the band picture. Instead, localised transitions within segments of the chain have to be invoked for emission as well as for absorption as evidenced by deconvoluted fluorescence excitation spectra characteristic of chromophores sitting in a random environment. Solid film spectra can be rationalised in terms of additional inhomogeneous broadening. In PDPV, yet not in PPPV, the excitation is strongly coupled to a chain deformation associated with a twist vibration of the biphenyl unit. In PPPV the observed Stokes shift is attributed to electronic relaxation in the course of energy transfer. The electron–phonon coupling parameters have been evaluated.

1. Introduction

Exciting an electron from the highest occupied to the lowest unoccupied level of an organic molecule generates an electron–hole pair that is strongly correlated because it is confined to the volume of the parent molecule. Owing to the weakness of the van der Waals interaction, this confinement is essentially preserved even in molecular crystals. Their elementary optical excitations are, therefore, Frenkel excitons. The k selection rule implies sharp transitions because the ground state is a $k = 0$ state. It breaks down in random organic phases where the exciton bands are split into a manifold of localised states mapped by the absorption profile and reflecting the built-in disorder (Jankowiak *et al* 1983).

At the other extreme are transitions among valence and conduction band states in covalently bonded semiconductor crystals, which give rise to more or less featureless absorption band profiles described by $\alpha \simeq (\hbar\omega - E_g)^n$, E_g being the band gap and n an exponent that depends on the band structure and dimensionality. Disorder manifests itself in the appearance of absorption tails, often exponential in energy (Cody *et al* 1981, John *et al* 1986).

By virtue of their structure, polymers can be considered as intermediates between a molecule and a semiconductor: the highest occupied and lowest

unoccupied molecular-orbital (HOMO and LUMO) states of the backbone chain form (filled) valence (Seki *et al* 1987) and (empty) conduction bands of essentially one-dimensional character because of weak inter-chain coupling. Exciton states are expected to occur below E_g (Friend *et al* 1987). The crucial quantity determining whether optical absorption ought to be described within the framework of the exciton or, rather, the band model is the strength of electron–hole correlation. Weak correlation with concomitant low binding energy of an electron–hole pair would favour the band approach. It is the widely accepted notion that the main optical transitions of the backbone of π-conjugated polymers like *cis*- or *trans*-poly(acetylene) (Lauchlan *et al* 1981), poly(*p*-phenylene) (Shacklette *et al* 1979, Bredas *et al* 1982), poly(thiophene) (Kaneto *et al* 1984, Taliani *et al* 1987), poly(pyrrole) (Kanazawa *et al* 1980) and poly(phenylenevinylene) (Wnek *et al* 1979, Bradley *et al* 1987, Bradley and Friend 1989) fall into this category. Onset of the absorption is believed to reflect the band gap. The exceptions to that rule are poly(diacetylenes) (PDA), for which optical and electrical studies (Lochner *et al* 1978) demonstrated that the lowest allowed transition is of excitonic origin, the band transition being much weaker and shifted by 0.4 eV towards higher energies (Sebastian and Weiser 1981).

The present paper critically examines the nature of the lowest optical transition of prototypical π-bonded polymers having non-degenerate ground states. The method employed is site-selective fluorescence spectroscopy (Personov 1983). Its ability to distinguish among different absorption routes rests on the following principles. Exciting a semiconductor with photons of energy $\hbar\omega > E_g$ creates free electrons and holes that relax quickly (<1 ps) to the band edges (Kaneto *et al* 1984) and, if the material is disordered, to tail states below E_g, thereby losing their memory about generation (Weinstein and Orlowski 1982). Luminescence originates from the recombination of localised electrons and holes, the recombination time depending on the e $\cdots$ h separation. The luminescence spectra will be independent of the excitation energy ν_{ex} yet shift to lower energy with increasing delay time between excitation and detection because electrons and holes that relaxed to deeper states of the density-of-states (DOS) distribution are farther apart and therefore recombine more slowly. Luminescence decay is non-exponential and extends over many decades in time (Noolandi *et al* 1980). For sub-band-gap excitation the emission spectrum can shift with ν_{ex} unless emission occurs from a common exciton state into which excitations collapse irrespective of their initial energy. By and large, these general features are borne out by the luminescence behaviour of chalcogenide glasses or amorphous silicon (Wilson *et al* 1985).

Within the framework of the localised excitation model, an excitation generated within a random solid phase executes an incoherent random walk within the manifold of hopping sites and relaxes energetically (Movaghar *et al* 1986). Eventually it may get stuck at a tail state if its decay rate exceeds the transition rate to a neighbouring site. This condition will be fulfilled for states below a demarcation energy called the localisation threshold ν_{loc}. Upon site-selective excitation one therefore expects luminescence to be emitted from states near ν_{loc}, i.e. independent of ν_{ex}, as long as the excitation energy ν_{ex} exceeds ν_{loc}. For $\nu_{ex} < \nu_{loc}$ emission will come from the absorbing site and, therefore, shift linearly with ν_{ex}, as illustrated by figure 1 (Cohen and Sturge 1982). It will, however, be resonant with the excitation only if the electron–phonon coupling is weak. Otherwise a Stokes shift will occur, reflecting the response of the medium to the creation of the electronic excitation. Luminescence decay is determined by the lifetime of the relevant excited states, which is typically of the order of nanoseconds. Some deviations from exponentiality may occur if emissions from different

species overlap. Upon measuring time-resolved spectra, one would see the emission spectra shift with time, monitoring spectral diffusion as long as $\nu_{ex} > \nu_{loc}$, while time-independent emission spectra are expected for $\nu_{ex} < \nu_{loc}$. Evidence for this behaviour has been derived from the spectral diffusion studies involving triplet excitations in a benzophenone glass (Lange *et al* 1988, Richert *et al* 1989) as well as singlet excitations in poly(vinylcarbazole) (Rockwitz and Bässler 1982, Rauscher and Bässler 1989). Application of site-selective low-temperature fluorescence spectroscopy to a matrix-isolated soluble PDA carrying a bis(phenyl acetate ester) substituent has also provided unambiguous support in favour of the concept of localised excited states subject to random walk among subunits of the backbone chain whose energies are slightly different because of chain distortion and random environment. Excitation above a localisation threshold ν_{loc}, within the inhomogeneous broadened absorption band yielded fluorescence bands invariant upon varying ν_{ex} while quasi-resonant behaviour was observed for $\nu_{ex} < \nu_{loc}$ (Rughooputh *et al* 1988).
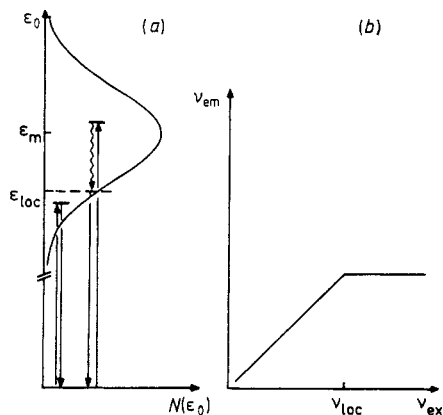

Figure 1. (*a*) Density-of-states profile of a random organic solid. States above the localisation threshold ε_{loc} are subject to incoherent random walk leading to energetic relaxation. States below ε_{loc} emit resonantly. (*b*) Schematic variation of the emission energy with excitation energy. To comply with spectroscopic convention, energies are denoted by wavenumber symbols.

The current belief that—with the exception of poly(diacetylenes)—polymers with π-conjugated backbone having non-degenerate ground states are appropriately described within the framework of semiconductor terminology rests on the observation of smoothly varying absorption tails, which, however, could well be due to a disorder-broadened localised transition, and luminescence bands (Bradley and Friend 1989, Feast *et al* 1985, Tokito and Saito 1986) exhibiting a Stokes shift of up to 0.9 eV. It is attributed to the radiative recombination of an electron–hole pair after relaxing to an excitonic polaron state localised on a single chain. Materials showing that behaviour are *cis*-poly(acetylene), poly(phenylenevinylene) (PPV) and poly(4,4'-diphenylenediphenylvinylene) (PDPV). Their optical properties seem, therefore, to differ from those of poly(diacetylenes) (PDA).

With this scenario in mind, we examined the low-temperature luminescence properties of two soluble conjugated polymers with bond alternation, poly(*p*-phenylenephenylvinylene) (PPPV and PDPV, embedded in low temperature 2-methyl-tetrahydrofuran (2MTHF) glasses employing site-selective laser excitation. The purpose of using matrix-isolated molecules is to eliminate inter-chain processes and thus ascertain the role of intra-chain processes for photoluminescence of these materials. The results support the concept of localised excitonic transitions, in both absorption and emission.

2. Experimental details

Two different samples of poly(phenylphenylenevinylene),
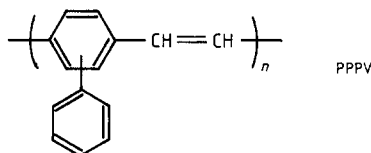
were synthesised via a Heck reaction. Their average molecular weight was 8000 and 2340, corresponding to a degree of polymerisation of 45 and 13, respectively. Poly(4,4′-diphenylenediphenylvinylene),
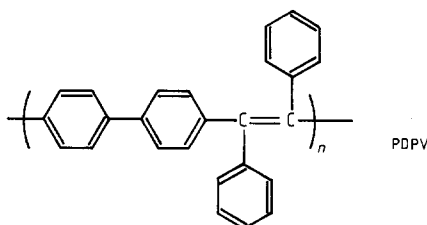
has been prepared by a condensation polymerisation described earlier (Feast and Millichamp 1983).

Both polymers are soluble in 2MTHF. Glasses have been prepared by cooling the solution at a rate of typically 2 K s^{-1} to a temperature of about 6 K. The concentration was adjusted to yield optical densities of order 10^{-1} and 1 for PPPV and PDPV, respectively. The optical path length was 0.2 cm. Fluorescence spectra were excited by a tunable excimer-laser-pumped dye laser of spectral bandwidth $0.15 \pm 0.05 \text{ cm}^{-1}$ and recorded with a high-resolution monochromator operated at a spectral resolution of a few wavenumbers.

3. Results

A family of fluorescence spectra of PPPV, parametric in excitation energy ν_{ex}, is shown in figure 2. It is obvious that the emission spectra vary with ν_{ex}, even if ν_{ex} exceeds $21\,000 \text{ cm}^{-1}$ (2.6 eV), usually considered to be the band gap. As ν_{ex} is scanned across the tail of the absorption spectrum (figure 3) towards higher energies, the emission spectrum shifts almost linearly with ν_{ex}. At a certain energy, which for the short-chain PPPV is about $22\,000 \text{ cm}^{-1}$, a second emission appears, red-shifted relative to the original spectrum by about 1100 cm^{-1}. It gradually gains in intensity upon increasing ν_{ex} further and finally replaces the original spectrum. This behaviour is illustrated in figure 4, delineating the variation of the $S_1 \rightarrow S_0$ 0–0 and 0–1 transitions of both spectra on the basis of the band assignment indicated in figure 2. Fluorescence spectra of the higher-molecular-weight sample are very similar except that the second emission feature already begins to show up above $\nu_{ex} = 21\,000 \text{ cm}^{-1}$. The variation of ν_{em} with ν_{ex} for the band system 1 approaches a linear law at low ν_{ex}, yielding a Stokes shift of only 200 cm^{-1}. Unfortunately the decrease of the luminescence intensity precludes reducing ν_{ex} further to check whether or not the emission would finally become resonant. Apart from some additional broadening and a red shift that depends on polymerisation conditions, the fluorescence spectra of poly(phenylenevinylene) films are very similar to the spectra of
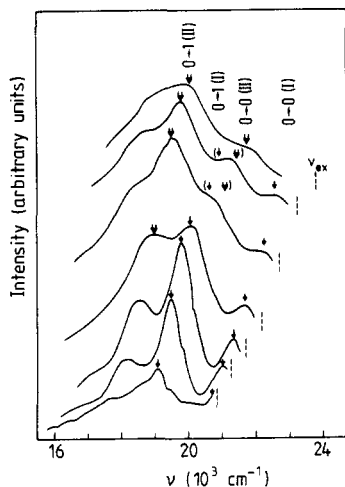
Figure 2. Fluorescence spectra of matrix-isolated PPPV parametric in excitation energy ν_{ex}. Single and double arrows are used to identify band systems I and II, respectively, each contributing a $S_1 \rightarrow S_0$ 0–0 and 0–1 transition.
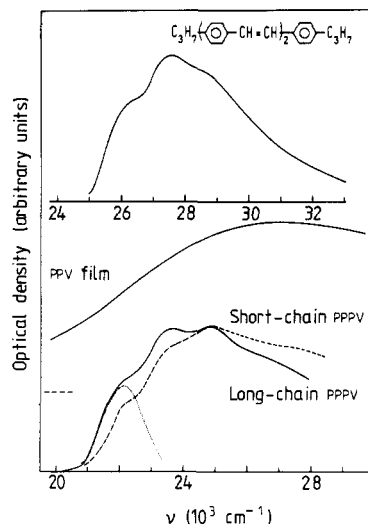

Figure 3. Absorption spectra of long-chain and short-chain PPPV in MTHF glasses (the dotted curve is a Gaussian profile mapping the distribution of electronic origins of the higher-molecular-weight sample), a PPV film (Bradley *et al* 1987) and the dimeric model compound bis(isopropylstyryl)-benzene (Berlman 1965).
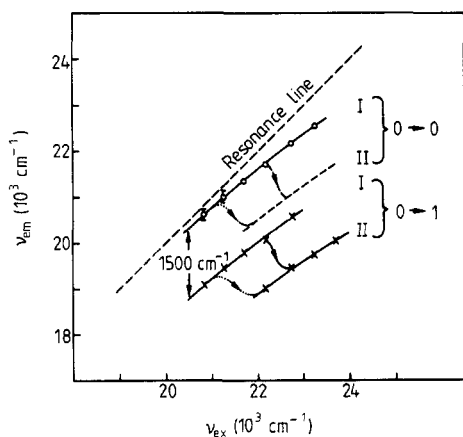

Figure 4. Shift of the $S_1 \rightarrow S_0$ 0–0 and 0–1 fluorescence maxima of band systems I and II upon varying the excitation energy. The dotted S-shaped transition line corresponds to the higher-molecular-weight samples.

matrix-isolated PPPV (Wong *et al* 1987) and virtually indistinguishable from that of a dimer model compound, bis(isopropylstyryl)benzene (BPSB) in liquid solution (Berlman 1965) (figure 5). The dominant vibronic peak appears 1550 cm^{-1} to the red of the $S_1 \rightarrow S_0$ 0–0 transition, carrying a shoulder at 1250 cm^{-1}. It is assigned to a convolution of a —C = C— stretch mode with modes of the phenyl ring of the chain. The similarity of the spectra confirms that the emission is characteristic of an isolated intra-chain chromophore and excludes the importance of lower-lying states generated by inter-chain aggregation as observed with poly(diacetylenes) (Wenz *et al* 1984).

Site-selectively excited fluorescence spectra of matrix-isolated PDPV, portrayed in figure 6, differ from PPPV spectra in several aspects: (i) The band width is significantly increased, preventing the resolution of vibronic structure. (ii) Except at the lowest
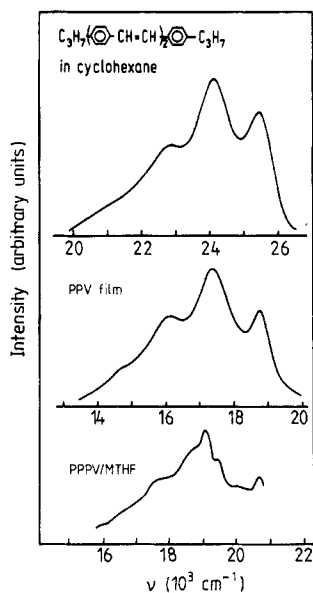
Figure 5. Comparison of the fluorescence spectra of BPSB in cyclohexane solution (Berlman 1965), of a PPV film (Bradley and Friend 1989) and of matrix-isolated PPPV upon exciting into the absorption tail.
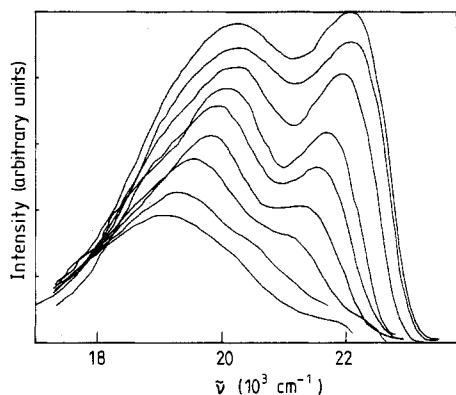

Figure 6. Fluorescence spectra of PDPV in MTHF glass, parametric in excitation energy.

excitation energy, two partially overlapping bands, henceforth assigned D1 and D2, can be distinguished, their relative magnitude depending on ν_{ex}. (iii) Upon increasing ν_{ex}, both bands shift with ν_{ex} yet become independent of ν_{ex} above 24 000 cm^{-1} (D1) and 23 400 cm^{-1} (D2), respectively, as illustrated in figure 7.

To identify the origin of the emission bands D1 and D2, fluorescence excitation (FE) spectra have been measured. Spurious features arising from the variation of the emission spectra with ν_{ex} have been eliminated by adjusting the energy difference between excitation and detection in accord with the $\nu_{em}(\nu_{ex})$ relation of figure 7. Plotting FE spectra for both emission bands on a logarithmic ordinate scale reveals structure arising from the superposition of three inhomogeneously broadened absorption bands (figure 8). This conclusion will be supported by a profile analysis below.

4. Discussion

4.1. PPPV fluorescence spectra

The variation of the fluorescence spectra of PPPV upon excitation above the 'band gap' of the π-electron states of the polymer chain, defined by the onset of absorption if plotted
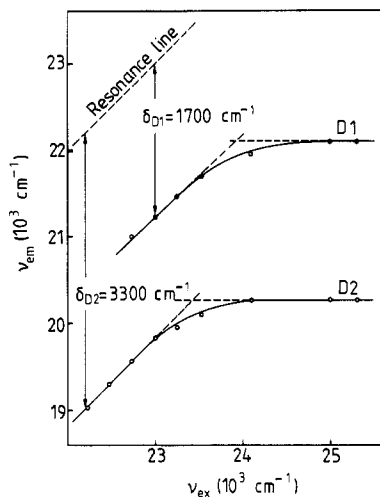
Figure 7. Variation of the maxima of the fluorescence bands D1 and D2 with excitation energy.
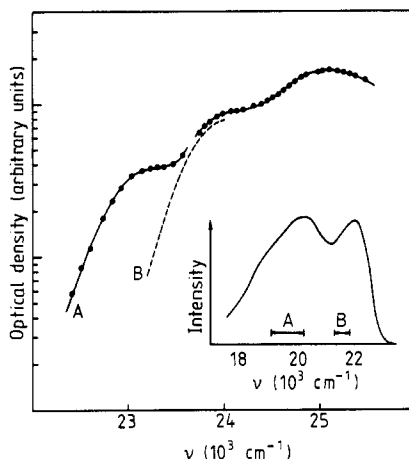
Figure 8. Excitation spectra of D1 and D2 emissions, monitored in the indicated spectral range. The break in the upper curve is due to a change of the dyestuff of the laser.

on a linear ordinate scale, is in striking disagreement with the band picture. Excitation into delocalised chain states should be followed by rapid electron–hole relaxation, leading to the population of a common emitting state. The present experiments clearly call for a localised description of both the emission and the absorption processes. This conclusion is further supported by an analysis of the absorption spectrum. The low-energy portion of the PPPV absorption spectra comprising their zero vibronic and first vibronic components is perfectly mapped by that of the dimeric model compound BPSB (Berlman 1965) after a red shift by 4000 cm^{-1} (figure 3). The low-energy shoulder of the $S_1 \rightarrow S_0$ 0–0 band can be fitted by a Gaussian having a full width at half-maximum (FWHM) of 1470 cm^{-1}, translating into a Gaussian width $\sigma = 625$ cm^{-1} (FWHM $= 2\sigma(2 \ln 2)^{1/2}$). It accounts for the disorder-induced fluctuation of the electronic transition energies. The red shift of the PPPV spectrum is attributed to the additional delocalisation of the excited state in PPPV over three or four monomer units (Hörhold and Opfermann 1970, Pomerantz *et al* 1989). The spectra also bear out the existence of a high-energy component that is more pronounced with the short-chain polymer. It can be assigned to chain segments of shorter effective conjugation length and present in greater proportion in the short-chain sample. The similarity of the absorption spectrum with that of a PPV film suggests that the latter should be described on the same premise if allowing for additional disorder-induced broadening of the electronic transition. The more or less featureless spectrum of absorption in the film cannot, therefore, be taken as evidence for a band-to-band transition, and neither can the energy difference between the band maximum and a fluorescence band be interpreted in terms of a conventional Stokes shift reflecting chain distortion after excitation.

Having established the localised character of the transition it is straightforward to discuss fluorescence spectra in terms of the framework of random organic solids, briefly outlined in the introduction. It implies the existence of an energy distribution of localised sites mapped by the $S_1 \rightarrow S_0$ 0–0 transition (Abrahams *et al* 1979). The sites are segments of the polymer chain comprising a few monomer units only. The width of the DOS reflects variations in both the zero-order energies due to fluctuations of the effective conjugation

length and the van der Waals interaction energies with the solvent. A localisation threshold ν_{loc} within the tail of the DOS separates states that participate in incoherent transport from states that do not. Excitations started at $\nu > \nu_{loc}$ will execute a random walk in the course of which they will on average relax to ν_{loc} and give rise to emission that is inhomogeneously broadened by spectral diffusion. States populated at $\nu < \nu_{loc}$ emit resonantly provided the response of the structure to a change in the electron distribution is weak enough to render zero-phonon (ZP) transitions observable. Their fractional intensity is determined by the Debye–Waller factor

$$I_{zp}/I_{tot} = e^{-S} \qquad (1)$$

S being the Huang–Rhys factor characterising the strength of the electron–phonon coupling of the localised transition. Numerically it is given by the ratio of the difference between vertical and adiabatic transition energies for either absorption or emission to the energy $\hbar\omega_{ph}$ of the dominant phonon. The ZP transition is accompanied by a phonon wing with Poisson-like intensity distribution,

$$g(n) = (S^n/n!)\,e^{-S} \qquad (2)$$

where n is the number of phonons coupling to an electronic transition. To analyse site-selective fluorescence spectra in the presence of disorder of the site energies, two limiting cases have to be distinguished:

(i) The distribution of the electronic origins, expressed by the distribution function $g(\nu)$, is broad relative to the width of the phonon wings of the homogeneous absorption and emission spectra of the sites. Then the fluorescence spectrum is the convolution of site absorption and emission profiles, each given by equation (2), because the laser excites sites having different electronic origins. For $S \geqslant 2$ the fluorescence band is dominated by the phonon wing, the displacement (Stokes shift) of the maximum relative to the laser energy being

$$\delta = 2S\hbar\omega_{ph}. \qquad (3a)$$

For larger S its shape approaches a Gaussian with Gaussian width

$$\sigma_{pw} = \hbar\omega_{ph}(2S)^{1/2}. \qquad (3b)$$

Hence

$$\delta/\sigma_{pw} = (2S)^{1/2}. \qquad (3c)$$

(ii) The fluctuation of site energies is much less than the width of the phonon wing. Then the single-site approximation is appropriate, yielding

$$\delta = \sigma\hbar\omega_{ph} \qquad \sigma_{pw} = \hbar\omega_{ph}(S)^{1/2} \qquad (4a)$$

and

$$\delta/\sigma_{pw} = S^{1/2}. \qquad (4b)$$

Inspection of the PPPV spectrum recorded upon exciting the bottom tail states of the DOS indicates (i) a small Stokes shift of $\delta = 200\ \text{cm}^{-1}$—much less than the width of the DOS—with tendency to decrease further upon lowering ν_{ex} and (ii) absence of pronounced phonon wings. This indicates weak electron–phonon coupling characteristic of S being of the order of 1, as usually found for molecular chromophores embedded in polymeric or, more generally, glassy environments (Bogner *et al* 1984, Kador *et al* 1986). The increase of δ with increasing ν_{ex} with concomitant broadening of the emission spectra is a signature of some spectral diffusion occurring (Jankowiak *et al* 1984). However, no threshold energy is discernible above which the emission becomes independent of excitation, as suggested by the random-walk concept. Instead, the emission

features double above a certain ν_{ex}, which depends on chain length. The plausible explanation is that, upon exciting higher-energy states within the DOS, an excitation may execute, say, one or two jumps until located at a site from where it can either make a Förster-type transition to a non-nearest neighbour before continuing its random walk or decay radiatively. The acceptor site will then emit its characteristic fluorescence. With increasing ν_{ex}, the probability for Förster transfer increases and the second fluorescence component will become the dominant one. The initial shift of both fluorescence emissions is dictated by the condition of optimising the spectral overlap between donor emission and acceptor absorption. Support for this explanation comes from the observation that the critical excitation energy for appearance of the low-energy fluorescence component depends on molecular weight. A donor state in a different environment will have the same transfer probability if the number of acceptor states in its neighbourhood is the same. Since transfer in a matrix-isolated polymer is restricted to individual molecules, it will occur at energies where the relative extinctions of both systems are equal. Since the ratio of the number of absorbing states per chain of the high- and low-molecular-weight samples is $3.5:1$, a bathochromic shift of the threshold energy for Förster energy in the high-molecular-weight sample by about $1000\ cm^{-1}$ is estimated on the basis of the measured low-energy tail of the absorption profiles. To determine Förster transfer radii requires knowledge of the coil structure of the polymer molecules, which is not available. We therefore abstain from speculative estimates.

In a condensed PPPV structure, realised in a PPV film, the density of low-lying acceptor states is significantly larger. Therefore excitations are able to relax to deeper states within the DOS by executing a random walk or by Förster transfer or a combination of both. This explains why the luminescence of PPV films is red-shifted relative to that of matrix-isolated PPPV molecules, although the spectral characteristics are virtually identical. The important implication is that the Stokes shift seen in these spectra is almost entirely determined by the energy loss that an excitation suffers in the course of migration and must not be taken as evidence for formation of an excitonic polaron.

4.2. PDPV spectroscopy

The fluorescence excitation spectrum of figure 8 can be deconvoluted into a system of three absorption bands, each of Gaussian shape and having Gaussian widths close to $400\ cm^{-1}$ (figure 9). They are assigned to two defects, D1 and D2, and the main-chain chromophore, M. Above $25\ 000\ cm^{-1}$ vibronic transitions overlap with the contribution of chain segments having shorter effective conjugation length. The absorption spectrum of a PDPV film included in figure 9 is readily generated from the spectrum of the matrix-isolated polymer molecule by increasing the inhomogeneous widths of the contributing bands. This observation reinforces the argument presented above against interpreting the spectrum in terms of a transition among delocalised band states of the conjugated polymer backbone.

Identification of the individual absorption bands is open to conjecture. It appears conceivable that one of the defect states or both are associated with an inter-chain phenomenon such as aggregation, which might occur in 10^{-4} to $10^{-3}\ mol/mol$ solutions in analogy to what is occurring in solutions of poly(diacetylenes) (Wenz *et al* 1984). An argument against this notion is that the ratio of defect to bulk absorption is about the same for the glassy solution and for the compact film, although one would expect chain interaction to be much stronger in the latter. Therefore it appears more likely that the different states are associated with chain segments of different effective conjugation
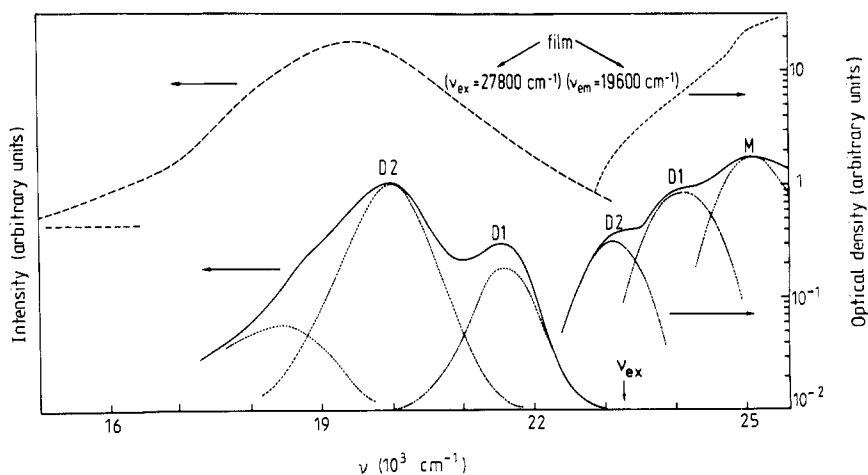
Figure 9. Right portion: Analysis of the fluorescence excitation spectra of PDPV in MTHF glass and of a PDPV film (Bradley *et al* 1987). Note the logarithmic ordinate scale. Left portion: Fluorescence spectra of PDPV in MTHF and solid film (Feast *et al* 1985), respectively. Deconvoluted D1 and D2 emission bands of matrix-isolated PDPV have been calculated on the basis of equation (2) for a phonon energy $\hbar\omega = 155\ \mathrm{cm}^{-1}$ and electron–phonon coupling parameters $S_{D1} = 11$ and $S_{D2} = 22$, respectively. The low-energy emission is the difference between the experimental and computed spectra.

lengths. For the purpose of identifying the nature of optical absorption and emission, this assignment is, however, irrelevant.

Upon site-selective excitation of D2 absorption states, emission band D2 is observed. It is characterised by a Stokes shift $\delta_{D2} = 3300\mathrm{cm}^{-1}$ and shifts linearly with ν_{ex} until ν_{ex} reaches the onset of D1 absorption at $23\,450\ \mathrm{cm}^{-1}$. D2 emission excited above that energy is independent of ν_{ex}, indicating that the emitting states are populated by energy transfer from D1 states. Directly excited D1 states have the options of emitting their characteristic D1 spectrum associated with a Stokes shift $\delta = 1700\ \mathrm{cm}^{-1}$ and shifting linearly with ν_{ex}, or converting non-radiatively to D2 states. As ν_{ex} reaches the onset of the M absorption band, the non-radiative decay route to D1 and D2 via energy transfer overrides the radiative channel. This explains both the absence of M emission and the saturation of ν_{em} (D2) above $24\,000\ \mathrm{cm}^{-1}$.

A summary of the PDPV absorption and emission bands is compiled in figure 9 together with the film emission spectrum. The latter can be considered as the convolution of D1 and D2 emission bands, exhibiting additional disorder broadening, and of an increased contribution of tail-state emissions also seen in the low-energy tail of the fluorescence spectrum of matrix-isolated PDPV. Obviously the higher density of states in the film provides additional low-lying acceptor states. However, the mutual shift of film and glass spectra is less than in the PPPV case. The likely reason is that due to strong localisation in PDPV (see below) excitation transport via random walk is excluded even in the film, the only channel for non-radiative relaxation being Förster transfer.

Although the overall Stokes shift contains a contribution due to energy transfer, there is clear evidence for the occurrence of conformational relaxation in PDPV following excitation, contrary to what has been observed with PPPV. To obtain an estimate of the strength of the electron–phonon coupling, we ignore the distribution of site energies relative to the relaxation energy and apply equations (4*a*) and (4*b*). This is justified by comparing the Stokes shifts associated with bands D1 and D2 and their inhomogeneous

band widths, respectively. From the value of δ_{D1} and δ_{D2} measured at low ν_{em} and from the widths of the emission bands ($\sigma_{pw,D1} = 550$ cm^{-1}, $\sigma_{pw,D2} = 700$ cm^{-1}), the ratios ($\delta/\sigma_{pw})_{D1} = 3.35$ and ($\delta/\sigma_{pw})_{D2} = 4.7$ are obtained, yielding $S_{D1} = 11$ and $S_{D2} = 22$ with constant phonon energies $\hbar\omega_{ph} = 155$ cm^{-1}. Recall that for PPPV an S value of order 1 has been obtained. Since phenyl substituents do not affect the electronic properties of the chain noticeably, this difference has to be attributed to the replacement of the phenylene group by the diphenylene group in the PDPV backbone. It is well known that the biphenyl molecule in the vapour phase has a twist mode with an estimated energy of 70 cm^{-1} (Stuart 1967). In the ground state the phenyl rings form an angle of about 20°. This is a compromise between steric repulsion and conjugation. In the excited state the gain in delocalisation energy overcompensates repulsion and the planar conformation is favoured. The potential energy surfaces of ground and excited states are therefore strongly shifted, giving rise to strong coupling of the electronic transition to the phenyl–phenyl twist mode. Its signature is the large Stokes shift in the absorption and fluorescence spectra of oligo(phenylenes), in both solution and single crystals. The fluorescence spectrum of crystalline *o*-terphenyl, which may serve as a model compound for a substituted biphenyl group embedded in a solid matrix, displays a broad structureless band with Gaussian width of about 900 cm^{-1} and subject to a Stokes shift of 5000 cm^{-1} (Onaka-Ito and Maruyama 1983). Hence $\delta/\sigma = 5.6$, yielding $S = 31$ and a phonon energy of 160 cm^{-1}, in good agreement with the above estimate.

We thus concur with Feast *et al* (1985) that in PDPV the excited state forms an excitonic polaron, yet discard the notion that it be formed by a pair of originally free electrons and holes, each forming polarons separately. Instead, both absorption and emission is properly described within a localised picture involving significantly displaced energy surfaces in ground and excited states. The absorption profile is identified as a superposition of different absorbing species, each subject to inhomogeneous broadening due to disorder and some homogeneous broadening due to phonon coupling.

5. Concluding remarks

The present spectroscopic studies are at variance with the concept of band-to-band transitions in π-conjugated backbone polymers with bond alternation. They demonstrate that absorption and emission spectra of PPV/PPPV and PDPV can consistently be interpreted in terms of the concept of disorder-mediated localised transitions involving relaxation via energy transfer. The results are in full accord with earlier results obtained for fluorescent poly(diacetylenes) (Rughooputh *et al* 1988). The distinguishing feature determining whether or not an excited state forms a polaron is the ability of the backbone to relax structurally into a state of lower energy. Adjacent phenyl rings embodied in the backbone have been shown to promote formation of an excitonic polaron, while the electron–phonon coupling in a mono(phenylenevinylene) chain is insufficient to cause structural relaxation. It is worth mentioning that the polaronic binding energy of the excitation is an order of magnitude larger than estimated for the polaron binding energy of a positive charge carrier in poly(*p*-phenylene) (0.03 eV, i.e. 250 cm^{-1}, Bredas *et al* 1982), without, however, considering the twist motion of the phenyl groups explicitly. Considering the stiffness of the chain, one might conclude that there is little if any structural relaxation in *cis*-poly(acetylene) as well. In fact, fluorescence spectra show a peak at the tail of the fluorescence excitation spectrum (Lauchlan *et al* 1981). It could well be explained in terms of excitation transport along the chain with subsequent

localisation at segments whose excitation energy is near to or below the demarcation energy separating transporting from non-transporting localised states.

PPPV and PDPV on the one hand and poly(diacetylenes) (PDA) on the other differ with respect to the mode of excitation transport. While excitation random walk along the distorted one-dimensional chain has been identified as the dominant transport mechanism in the latter, Förster transfer prevails in the former systems if matrix-isolated. This difference can be traced back to morphology and strength of electron–phonon coupling. Formation of an excitonic polaron, e.g. in PDPV, is a process occurring on the timescale of an elementary transfer act (or is even faster) and thus excludes multiple-step transport. Förster transfer and random walk, on the other hand, are competitive processes. The former requires spectral overlap among chromophores. It is unfavourable among the segment of an elongated or weakly distorted chain, such as a fairly rigid PDA chain, where the transition moments of the elements are parallel to the chain, yet can occur within a polymer molecule such as PPPV that is likely to assume a coil form in solution.

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References

Abrahams E, Anderson P W, Lisciardello D C and Ramakrishnan T V 1979 *Phys. Rev. Lett.* **42** 673
Berlman J B 1965 *Handbook of Fluorescence Spectra of Aromatic Molecules* (New York: Academic)
Bogner U, Beck K, Schätz P and Maier M 1984 *Chem. Phys. Lett.* **110** 528
Bradley D D C, Evans G P and Friend R H 1987 *Synth. Met.* **17** 651
Bradley D D C and Friend R H 1989 *J. Mol. Electron.* **5** 19
Bredas J L, Chance R R and Silbey R 1982 *Phys. Rev.* B **26** 5843
Cody G D, Tiedje T, Abeles B, Brooks B and Goldstein Y 1981 *Phys. Rev. Lett.* **47** 1480
Cohen E and Sturge M D 1982 *Phys. Rev.* B **25** 3828
Feast J W and Millichamp I S 1983 *Polym. Commun.* **24** 102
Feast J W, Millichamp I S, Friend R H, Horton M E, Phillips D, Rughooputh S D D V and Rumbles G 1985
    Synth. Met. **10** 181
Friend R H, Bradley D D C and Townsend P 1987 *J. Phys. D: Appl. Phys.* **20** 1367
Hörhold H H and Opfermann K 1970 *Macromolecules* **131** 105
Jankowiak R, Ries B and Bässler H 1984 *Phys. Status Solidi* b **124** 363
Jankowiak R, Rockwitz K D and Bässler H 1983 *J. Phys. Chem.* **87** 552
John S, Soukoulis C, Cohen M H and Economou E N 1986 *Phys. Rev. Lett.* **57** 1772
Kador L, Schulte G and Haarer G 1986 *J. Chem. Phys.* **90** 1264
Kanazawa K K, Diaz A F, Gill W D, Grant P M, Street G B, Gardina G P and Kwak J F 1980 *Synth. Met.* **1**
    329
Kaneto K, Kohno Y and Yoshino K 1984 *Solid State Commun.* **51** 267
Lange J, Ries B and Bässler H 1988 *Chem. Phys.* **128** 47
Lauchlan L, Etemad S, Chung T-C, Heeger A J and McDiarmid A G 1981 *Phys. Rev.* B **24** 3701
Lochner K, Bässler H, Tieke B and Wegner G 1978 *Phys. Status Solidi* **88** 653
Movaghar B, Grünewald M, Ries B, Bässler H and Würtz D 1986 *Phys. Rev.* B **33** 5545
Noolandi J, Hong K M and Street R A 1980 *Solid State Commun.* **34** 45
Onaka-Ito T and Maruyama T 1983 *Mol. Cryst. Liq. Cryst.* **91** 187
Personov R I 1983 *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems* ed. V M Agrano-
    vich and R M Hochstrasser (Amsterdam: North-Holland) p 535

Pomerantz M, Cardona R and Rooney P 1989 *Macromolecules* **22** 308
Rauscher U and Bässler H 1989 *Macromolecules* **22**, at press
Richert R, Bässler H, Ries B, Movaghar B and Grünewald M 1989 *Phil. Mag. Lett.* **59** 95
Rockwitz K D and Bässler H 1982 *Chem. Phys.* **70** 307
Rughooputh S D D V, Bloor D, Phillips D, Jankowiak R, Shütz L and Bässler H 1988 *Chem. Phys.* **125** 355
Sebastian L and Weiser G 1981 *Phys. Rev. Lett.* **46** 1156
Seki K, Asada S, Mori T and Inokuchi H 1987 *Synth. Met.* **17** 629
Shacklette L W, Chance R R, Ivory D M, Miller G G and Baghnan R H 1979 *Synth. Met.* **1** 307
Stuart H A 1967 *Molekülstruktur* 3rd edn (Heidelberg: Springer)
Taliani C, Danielli R, Zambioni R, Ostaja P and Porzio W 1987 *Synth. Met.* **18** 177
Tokito S and Saito S 1986 *Macromol. Chem. Rapid. Commun.* **7** 557
Weinstein B A and Orlowski T E 1982 *Phys. Rev. B Rapid Commun.* **26** 4777
Wenz G, Muller M A, Schmidt M and Wegner G 1984 *Macromolecules* **17** 837
Wilson B A, Kerwin T P and Harbison J P 1985 *Phys. Rev. B* **31** 7953
Wnek G N, Chien J C W, Karasz F E and Lillya C P 1979 *Polymer* **20** 1441
Wong K S, Bradley D D C, Hayes W, Ryan J F, Friend R H, Lindenberger H and Roth S 1987 *J. Phys. Chem.* **20** L187