PHYSICAL REVIEW B **68**, 125202 (2003)

Recombination of triplet excitons and polaron pairs in a derived paraphenylene vinylene pentamer

J. De Ceuster,[1] E. Goovaerts,[1] A. Bouwen,[1] and V. Dyakonov[2]
[1]*Physics Department, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium*
[2]*Energy and Semiconductor Research, University of Oldenburg, Carl von Ossietzky Str. 9-11, D-26121 Oldenburg, Germany*
(Received 2 April 2003; published 10 September 2003)

The triplet photoexcited states of the pentamer 2,5-di-*n*-octyloxy-1,4-bis (4',4''-bisstyryl)styrylbenzene in a polystyrene matrix have been investigated by optically detected magnetic resonance (ODMR) spectroscopy in spin coated films at different concentrations of the blend. As previously reported for related *para*-phenylene vinylene (PPV) polymers, a part of the singlet excitons—the primary photoexcitations—are dissociating by intermolecular charge transfer, which results in Coulomb bound pairs of charge carriers, the distant polaron pairs (PPs). At low temperature and weak photo-excitation, however, the triplet exciton (TE) ODMR spectrum is dominant relative to that of the PPs, which points to a more efficient formation of the long living TEs than in PPV polymers. From a detailed analysis of the TE spectrum a rhombic ($D=0$, $E=0.037\ \mathrm{cm}^{-1}$) zero-field splitting interaction could be determined. Under optical excitation a much faster saturation of TE compared to PP spectra is found, in qualitative agreement with the previously proposed triplet-triplet annihilation mechanism for ODMR. A quantitative analysis shows a stronger than expected intensity dependence at higher excitation levels, which is attributed to an increasing probability for triplet-triplet annihilation as a result of the decreasing average distance between pairs of triplet excitons. Furthermore, the PP signal shows a much faster response than that of the TEs ($\tau=0.22$ and 1.2 ms, respectively, measured at 2.5 K), which also calls for a refinement of the description of the processes involved. TE and PP signals also show markedly different behaviors under a variation of the oligomer concentration in the polystyrene matrix, and of the measuring temperature. These results are discussed in light of the different formation and recombination mechanisms of excitons and polarons in conjugated organic materials.

DOI: 10.1103/PhysRevB.68.125202 PACS number(s): 71.35.−y, 71.38.−k, 78.66.−w

I. INTRODUCTION

Considering the fast growing number of applications of organic semiconductors in the last years, it is increasingly important to study the basic physics of the materials and devices on which they are based. Both for light emitting diode and solar cell applications the knowledge of and the possibility to control the occurring photoexcited states can lead to improved device efficiencies. Previous studies have demonstrated the existence of intrachain and interchain charge carriers in both singlet and triplet state.[1–3] According to experimental findings, the photoexcitation of conjugated polymers generates intrachain singlet excitons (SEs), i.e., pairs of electrons and holes with opposite charges and antiparallel spins bound by the Coulomb attraction. Exciton decay occurs through radiative and nonradiative processes. The radiative decay of excitons results in photoluminescence (PL), and in some materials the PL quantum efficiency can reach values of over 90%.[4,5] The reactions that involve those neutral excitations in conjugated polymers are very intriguing. By studying the dependence of the PL on the conjugation length of the polymers (or oligomers), it was found that the PL is redshifted as the length of the oligomers increases, which means that the SE is an intrachain excitation and extends over the whole conjugation segment, consisting of up to 6–7 monomers in length.[6] Once formed, a SE can be transformed into a triplet *intrachain* exciton via intersystem crossing (ISC). The intrachain triplet exciton (TE), in contrast to the singlet one, is much more localized, being in size not larger than the benzene ring in conjugated *para*-phenylene vinylenes (PPV),[1] and as a result is less sensitive to the oligomer size. This is in agreement with theoretical investigations performed on oligo(phenylenevinylene).[7] Radiative decay from the TE state is generally forbidden. Recently Romanovskii *et al.*,[8] however, have experimentally demonstrated the presence of delayed fluorescence and phosphorescence in ladder-type methyl-poly(*para*-phenylene) and PPV by time-resolved PL and modulation spectroscopy. Also, Partee *et al.*[9] have provided strong evidence for a significant contribution to the singlet emission resulting from triplet-triplet annihilation into singlet states.

Alternatively, the SE can decay via electron transfer onto a neighboring chain, or to a next conjugated segment of the same chain. This process forms a charge-transfer (CT) interchain or an interconjugated segment exciton, sometimes called a polaron pair (PP).[10] From the neighboring site, the mobile polaron can hop to a further chain or segment while still belonging to the pair, at least at distances not exceeding the Coulomb interaction radius. This pair is called a *geminate* pair to emphasize the common origin of negative and positive charges (polarons), in contrast to a *nongeminate* PP which is formed by charges donated by different parents excitons. Note that this occurs in a 3-to-1 ratio triplet to singlet, while predominantly singlet states are formed from geminate pairs. This issue on the formation of geminate pairs and/or nongeminate pairs is closely related to the discussion on the nature of primary excitations in conjugated polymers.[11] Polaron pairs were introduced to account for the magnetic field effect on photoconductivity.[10] Later, they were invoked to explain long-lived states observed in photo-induced absorption.[12] Most recently, Müller *et al.* performed two-step photoexcitation experiments on a photodiode based on a ladder-type conjugated polymer.[13] They ascribed the increase in photocurrent in the second step to dissociating PPs. Thus, PPs may be considered as a common phenomenon in semiconducting polymers. PPs are important intermediate states that exist between electronic molecular excitations and free charge carriers. Their formation is very important for the fate of injected and/or photogenerated charges in organic semiconductors. Since the use of conjugated polymers/oligomers in organic light emitting diodes is directly related to their PL efficiency, the photoinduced charge transfer should be prevented. The latter leads to the dissociation of the primary photogenerated SEs, which are responsible for the light emission. Nevertheless, the status of the PP as a quasiparticle leads to a certain controversy both in the literature and discussions, especially if one attempts to assign certain bands in the optical spectra to PPs. The situation, however, is very different in magnetic resonance experiments. Electron paramagnetic resonance (EPR) and in particular optically detected magnetic resonance (ODMR) have already been shown to be powerful techniques in this field of investigation.[1–3,14–19] In ODMR, the recombination of spins in pairs is responsible for the effects observed. This process involves pairs of charges (short-living or long-living) just by definition. These experiments contributed to demonstrate the existence of polarons, PPs, and TEs. At least at the first stage, they were of purely fundamental interest and had little relevance to the broad efforts to improve the efficiency of organic light emitting diodes (OLEDs).

Now, more than a decade after the first publication,[20] the OLED research activities have almost moved out of the research lab into the industrial sector and address more technological aspects.[21,22] Moreover, the production of OLED displays became a reality.[23] At the same time, the questions of how to "violate" spin statistics and create more singlet excitations than the expected 3-to-1 ratio by means of electrical injection of charges became more and more challenging. The validity of the spin statistics has been doubted in a recent paper by Wilson *et al.*[24] Related to this, the so-called electrophosphorescence process is nowadays of great interest. It was demonstrated that the external quantum efficiency of the OLED can be improved to 8% by the introduction of "heavy" atoms in the molecule.[25,26] This increases the spin-orbit coupling and forms more triplet excitations, which in turn decay radiatively (phosphorescence), or annihilate in a second order reaction and produce singlet excitations. In this context, fundamental investigations of spin-dependent recombination processes, e.g., the singlet and TEs transformation mechanisms occurring in the device active layer, may lead to new approaches in an area once considered as one of purely applied research. Compared to polymers, significantly different properties can be expected in oligomers in which the conjugated segments are shorter and well defined, and the intermolecular interactions can can be altered by their concentration in a nonconjugated matrix.

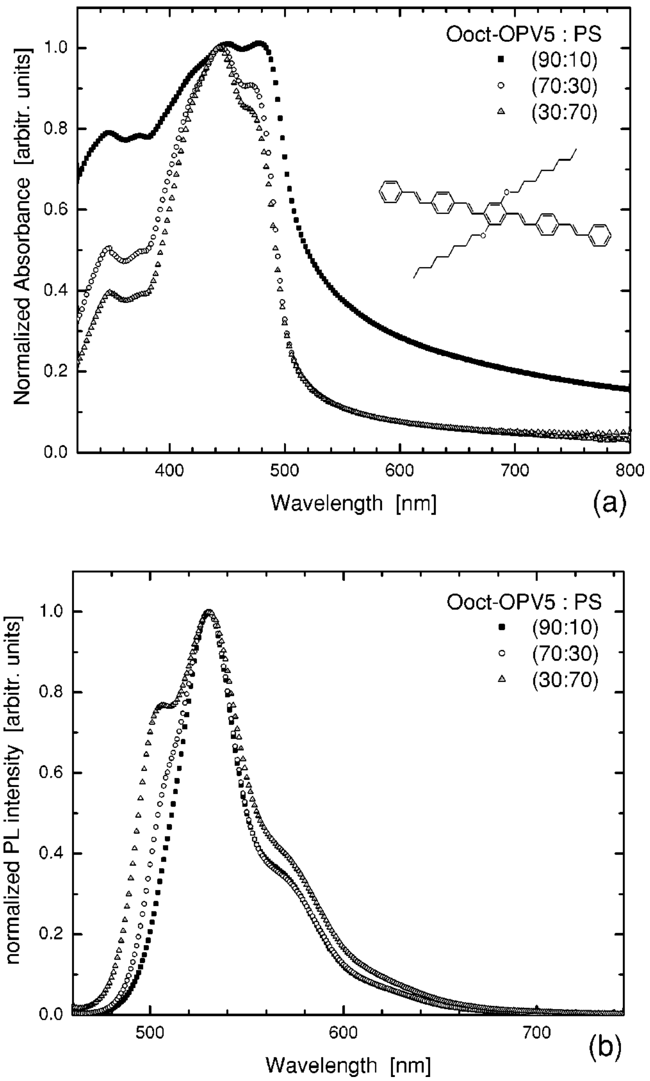

FIG. 1. Normalized optical absorption (a) and photoluminescence (b) of spin-coated films of Ooct-OPV5 in PS at three different concentrations: (90:10), (70:30), and (30:70); $T=293$ K. The inset shows the chemical structure of the conjugated molecule.

In this work we present ODMR measurements on a *para*-phenylene vinylene derived oligomer blended at different concentrations with polystyrene. Detailed information on the nature, and on the formation and decay of the triplet excitations in this system is obtained by variations of the photoexcitation level, temperature, and concentration, and this will be discussed in the framework of the triplet-triplet annihilation model. One of the aims of this work is to further clarify the effects of morphology and intermolecular distance on charge transfer phenomena and spin dynamics.

II. EXPERIMENT

The investigated conjugated molecule is the oligo(*p*-phenylenevinylene) (OPV) derivative, 2,5-di-n-octyloxy-1,4-bis (4',4''-bisstyryl)styrylbenzene, shortly denoted as Ooct-OPV5 (see the inset to Fig. 1). This oligomer, synthesized by Gill *et al.*,[27] has a fixed length of five phenyl units and is substituted for by two octyloxy chains on the middle phenyl unit, which increase the solubility. It emits a bright greenyellow PL band centered at 530 nm. Solutions of Ooct-OPV5 and polystyrene (PS) were prepared in different concentrations (30:70), (70:30), and (90:10) (weight ratios) using chloroform ($CHCl_3$) as a solvent. To start, a 0.5-wt % solution was made of PS in the solvent whereafter appropriate concentrations of Ooct-OPV5 were added. From these solutions the films were spin coated on glass substrates (at 3500 rpm over 40 s). The nonconjugated PS, which serves here as a transparent matrix for the Ooct-OPV5 molecules, makes it possible to obtain homogeneous films, and is known to favor charge transfer processes, in contrast to other polymers such as polyethylene.[19]

X-band ($\nu \approx$ 9.4 GHz) ODMR experiments were performed in a Bruker ESP300 spectrometer with an Oxford liquid helium flow cryostat ($T = 2 - 300$ K). The sample is on a holder with optical fiber access for optical excitation, and the photoemission is collected through the optical windows of the rectangular cavity and imaged onto a silicon photodetector. The microwave induced change in the PL intensity ΔI_{PL} was detected with a lock-in amplifier (EG&G 7220), while chopping the microwave power (on/off modulation). The PL intensity I_{PL} was measured independently with the same photodetector during these procedures. As the ODMR signal we will further consider the relative quantity $S_{ODMR} = \Delta I_{PL}/I_{PL}$, i.e., the relative value of the microwave-induced modulation of the PL intensity. All ODMR measurements were performed at 2.7 K except as otherwise stated, and laser light at 476 nm was employed for optical excitation. Optical absorption and photoluminescence were measured in a Varian Cary 5 UV-VIS-NIR spectrophotometer and Varian Cary Eclipse spectrometer, respectively.

III. RESULTS AND DISCUSSION

A. Absorption and photoluminescence

The optical absorption and PL spectra of spin-coated films with different concentrations were recorded (Fig. 1). First, the normalized absorption curves in Fig. 1(a) will be discussed. The sample (90:10) has a lower content of PS compared to (70:30) and (30:70) and, therefore, the films forming properties are less good. In this sample, the vibronically broadened main absorption band centered at 450 nm shows a redshift of about 0.05 eV with respect to the other samples. This can be an indication of aggregate formation. The position of the high-energy absorption band centered at 345 nm is not affected by the oligomer concentration. The PL spectra [see Fig. 1(b)] were taken with an excitation wavelength of 450 nm. Qualitatively, the PL intensity increases with increasing oligomer concentration. The PL in conjugated molecular system originates from SEs. The curves for the three samples show similar shapes. At the high energy side the Stokes band corresponding to the 0-0 transition becomes more pronounced for the films with lower concentration of oligomer. This 0-0 transition is the transition between the lowest vibrational levels in both the lowest unoccupied and highest occupied molecular orbitals. The reason for the relative changes can be attributed to reabsorption in the films with higher density of molecules.

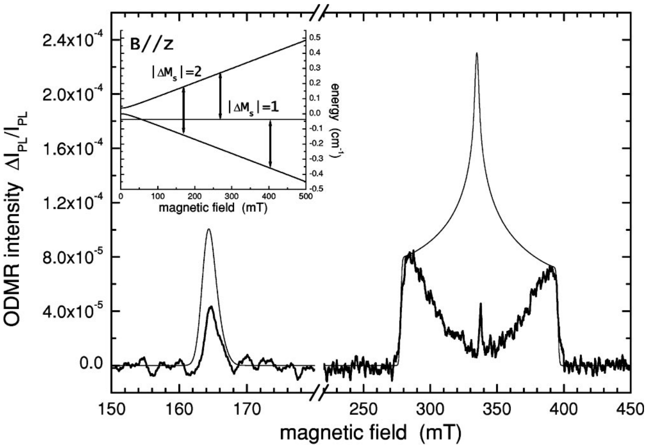

FIG. 2. ODMR spectrum of a spin coated film of Ooct-OPV5 in PS (90:10). $T = 2.7$ K, $\lambda_{exc} = 476$ nm, and $P_{\mu w} = 200$ mW. The powder EPR simulation of the spectrum is shown for comparison.

B. Optically detected magnetic resonance in Ooct-OPV5:PS blends

The microwave induced changes in the PL intensity in blends of Ooct-OPV5:PS as the magnetic field was swept are shown in Fig. 2. Three features can be distinguished, each corresponding to a microwave induced *increase* of the PL intensity. A narrow peak of $\Delta H \approx 3.5$ mT width occurs at a magnetic field of about 340 mT, corresponding to a g factor close to the free electron g value. Symmetrically on both sides of this, two signals with a splitting between the maxima of about 100 mT can be clearly observed, and are ascribed to the $\Delta M_S = \pm 1$ transitions between the Zeeman sublevels of an anisotropic paramagnetic triplet state. Finally, a so-called "half-field" transition at a magnetic field of ± 165 mT ($g_{eff} \approx 4$) is also discerned, which is considered as a signature for the presence of triplet spin systems.[15,28] The overall spectrum results from an average over the orientational distribution of the molecules in the spin coated film, comparable to a powder EPR spectrum.

1. *Triplet exciton spectrum*

As previously reported for PPV compounds,[18] the triplet powder pattern and the half-field transition originate from the TEs, which can eventually be formed through direct ISC from the excited singlet state, or via intermediate PP states. The latter are resulting from the dissociation of SEs. Both purely axial and rhombic cases of the zero-field splitting term (zfs) $\mathcal{H}_{zfs} = DS_z^2 + E(S_x^2 - S_y^2)$ in the spin Hamiltonian, corresponding to $D \neq 0, E = 0$, and $D = 0, E \neq 0$,[29] respectively, have been reported for different PPV-type polymers and oligomer blend systems[15]. In the present case, the positions of the half-field transition and the edges of the triplet powder spectrum in the $g = 2$ region can be obtained simultaneously only in the assumption of a near-orthorhombic interaction.[29] This leads to zfs parameters $D \approx 0$ and $E = 0.037 \pm 0.002$ cm^{-1} which were used to simulate the powder EPR spectrum superimposed on the experimental ODMR spectrum in Fig. 2. Both the position and asymmetry of the half-field transition are well reproduced. However, the shape of the TE spectrum in the $g=2$ region deviates quite strongly from the simulation. Here the difference between EPR and ODMR intensities must be taken into account: while the EPR intensity is given by the probabilities of the magnetic dipole transitions between the spin states (induced by the magnetic field component of the microwaves), additional elements have to be taken into account in order to describe the changes in SE PL intensity resulting from the transitions between TE spin states. This can lead to important differences in the EPR and ODMR contributions to the powder spectrum as a function of the molecular orientation. An explicit derivation of this orientational dependence in the latter case can only be obtained from a validated model of the ODMR mechanism, which is as yet not available. In the present case the ODMR contributions are strongly suppressed for orientations of the molecule in which the magnetic field direction is close to the principal axis for which the D value is zero. Reasons for this can include the dependence of relaxation times and of TE decay probabilities as functions of the molecular orientation, combined with film morphology effects. The latter are presently under further investigation

While both axial and orthorhombic cases of the zfs have been previously reported in literature,[15] a pure rhombic analysis was already put forward for poly-(2,5-dihexoxy-PPV) (DHO-PPV) studied by Swanson *et al.* ($D'=3E'=0.0487\ \mathrm{cm}^{-1}$ or 52.1 mT, which is equivalent to $D=0$, $E=2E'=0.0325\ \mathrm{cm}^{-1}$),[1]who also found a better fit for the half-field transition in this assumption. The reported spectra of DHO-PPV evolve towards the shape for the orthorhombic EPR simulation at higher temperatures ($T>50$ K).[1] At these temperatures no ODMR signals of the TE can be observed in our Ooct-PPV:PS films (see Sec. III C). Interestingly, in DHO-PPV, the phenyl rings are substituted with alkoxy groups in *para* positions, similar to the central ring of the Ooct-PPV pentamer. This suggests that the octyloxy substitution is responsible for the orthorhombic zfs interaction, and that the triplet exciton is localized mainly on this substituted central ring in this PPV pentamer.

2. Origin of the TE ODMR

The relative intensity of TE ODMR spectrum vs the PP peak is unusually high in the Ooct-OPV5:PS blends as compared to observations of triplets in other conjugated systems.[1,2,16,28] The visibility of triplet molecular excitons in a PL originating from the radiative decay of SEs is indeed quite unusual. In the samples studied here, no radiative decay of TEs (phosphorescence) was observed, similar to the observation in most PPV-derivatives. Triplet excitons either decay nonradiatively to the ground state or can be converted to other excited states. EPR transitions between the TE states are found to influence the PL intensity and to give rise to the TE ODMR. Three spin-dependent recombination models have been proposed for this: (i) triplet-triplet (T-T) annihilation,[3,28,30] (ii) triplet-singlet quenching,[2] and (iii) ground state depopulation due to long-living excited triplet state.

In the *T-T annihilation model*, two TEs, close to each other, can couple and form a pair with a combined energy which is sufficient to create a SE. This pair of TEs has singlet, triplet, and quintuplet states. At resonance, the microwaves increase the population of the singlet state, from which a SE can be formed with spin conservation, leading to an increase of the steady state PL yield.

In the *quenching model*, TEs close to SEs quench the PL from the latter. At resonance, the triplet decay rate will increase therefore decreasing the quenching effect. The *ground-state depopulation model* is self-explanatory and leads to a less efficient photogeneration of SEs, which may be altered by resonant microwaves if the final spin states of the TEs display a faster decay to the ground state.

3. Narrow ODMR line

The second contribution to the spectrum, a narrow peak at 340 mT ($g=1.9825$), originates from microwave induced recombination between positive and negative polarons. These distant, but still Coulomb interacting, charge carriers form so-called polaron pairs and are formed in a charge transfer reaction through dissociation of SEs. Initially these geminate PPs predominantly are in a singlet spin state. The very formation of these pairs lowers the PL intensity and is therefore undesirable for light emitters based on conjugated molecules. Alternatively, the PPs can be formed by the interaction between two (nongeminate) polarons originating from different excitonic states, in which case triplet and singlet states are expected to be statistically represented. At low excitation levels mainly geminate pairs are present because on average the *intrapair distance* is much less than the *interpair distance*. When the polaron concentrations are increased, the pair formation with polarons originating from different SEs becomes very important when this inequality is challenged. Eventually, resonant microwaves act on the spin state of (one of) the charge carriers in the PP, which opens a recombination channel and increases the PL intensity. The nature of this mechanism, which leads to the ODMR observation of the charge transfer states, is not straightforwardly determined.

To shed light on this issue as well as to prove the CT character of the SE dissociation, we performed ODMR experiments at several relative concentrations of the conjugated molecule in the blend (see Sec. III. E). Indeed, the probability for creation of PPs in a CT process obviously depends on intermolecular distances. In pure conjugated polymers[1,2,28] this distance is hard to control and is mainly determined by more or less bulky side groups. The shorter this distance, the lower the threshold for hopping. It is known, for conjugated polymers blended in a PS matrix, that the CT will only occur up to a critical intermolecular distance, after which only the energy transfer will be operative for energy dissipation.[19,31] The formation of aggregates, or crystalline regions, in concentrated blends and in pure polymers, on the other hands, would enable the charge transfer. Note that in ODMR one indirectly detects the resonant microwave transitions between the states of the triplet PPs via their influence on the SE PL intensity.

C. Frequency and temperature dependence

Figure 3 shows the ODMR intensity for PPs and TEs as a function of the frequency of the amplitude modulation of

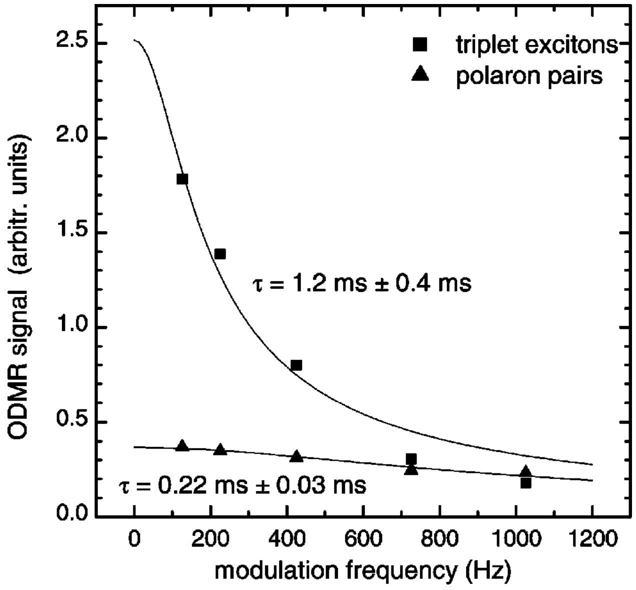

FIG. 3. ODMR intensity as a function of the modulation frequency of the modulated microwaves. [(30:70) sample, $T=2.7$ K, $\lambda_{exc}=476$ nm, and $P_{\mu w}=200$ mW]. The calculated frequency dependence is shown for comparison (see to text).

microwaves. The phase of the lock-in amplifier was always tuned to maximize the signal intensity. When the modulation frequency becomes larger than the reciprocal lifetime of the excited states, the signal intensity starts decreasing. Clearly a different frequency response is measured for PPs than for TEs. The contribution of PPs to the SE emission has a faster response than that of the TEs. From simulations of the data points in Fig. 3, an estimation for the TE and PP response times could be made. The lifetime of TEs in PPV at low temperatures was measured to be in the range of millisecond,[28,32] and in poly(2-phenyl- 1,4-phenylenevinylene) (PPPV) polymer films a clear difference in response times was reported between TEs and PPs, $\tau=1.25$ ms and ± 0.55 ms, respectively.[16] A faster decay ($\tau \approx 100$ μs) was observed in polymer films or frozen solutions of 2,5-dihexoxy and 2,5-octoxy substituted PPV (DHO-PPV and DOO-PPV) by modulated PL spectroscopy.[9]

Assuming an exponentially decaying response with characteristic time τ and a rectangular on/off modulation of the microwaves, one finds, after Fourier spectral analysis for the amplitude,

$$R(\omega)\propto \frac{\tau^2}{\sqrt{1+\omega^2\tau^2}},$$

which is measured by means of the lock-in detector. From the best fits of the data to this frequency dependence, a value of $\tau_{TE}=1.2$ ms (± 0.4 ms) was derived for the TEs and an approximately five times shorter response time of $\tau_{PP}=0.22$ ms (± 0.03 ms) for the PPs, in qualitative agreement with the cited poly-PPPV results.[16]

In the *T*-*T* annihilation model, the triplet PPs recombine to form TEs as an intermediate state and this contributes indirectly to the SE emission and the ODMR signal. In a straightforward interpretation, the response time of the PP ODMR would be larger than or equal to that of the TE signals, which is in contradiction with the present observations and the results of Ref. 16. Therefore, a refinement of the model is required which either considers additional pathways for the PP contribution to the ODMR signal, or gives a more precise description of the evolution of the spin states throughout the consecutive processes of PP to TE conversion and *T*-*T* annihilation. This will be further discussed in Sec. III D.

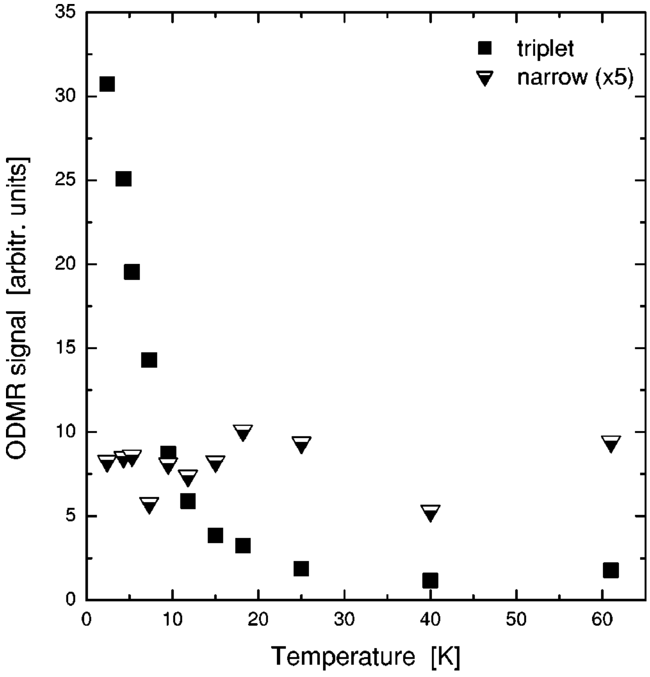

FIG. 4. ODMR intensity as a function of temperature, $P_{exc}=120$ mW, $\lambda_{exc}=476$ nm, and $P_{\mu w}=200$ mW).

The ODMR intensities as a function of temperature are shown in Fig. 4. A fast decrease of the intensity of the TE signal with temperature is observed and the triplet spectrum is vanishing above 20 K. This strong decrease is mainly ascribed to decreasing spin-lattice relaxation times, combined with the effect of the Boltzmann distribution between the triplet spin levels. The diffusion of TEs to find a partner for annihilation or quenching would be expected to become more effective and to increase the TE signal. This effect clearly cannot compete with the previous detrimental effects. Unfortunately, this does not give any clear arguments to discriminate between the different spin-dependent recombination models.

As concerns the PPs, there is little or no change of intensity with increasing temperature. This rules out the possibility of free polaron recombination, as also found in the polymer case.[28] Indeed, for this spin-dependent recombination model, a $1/T^2$ dependence would have been expected, according to

$$\frac{\Delta I_{PL}}{I_{PL}}=P_{P+}\cdot P_{P-}\approx\left(\frac{g\mu_B B_0}{2kT}\right)^2,$$

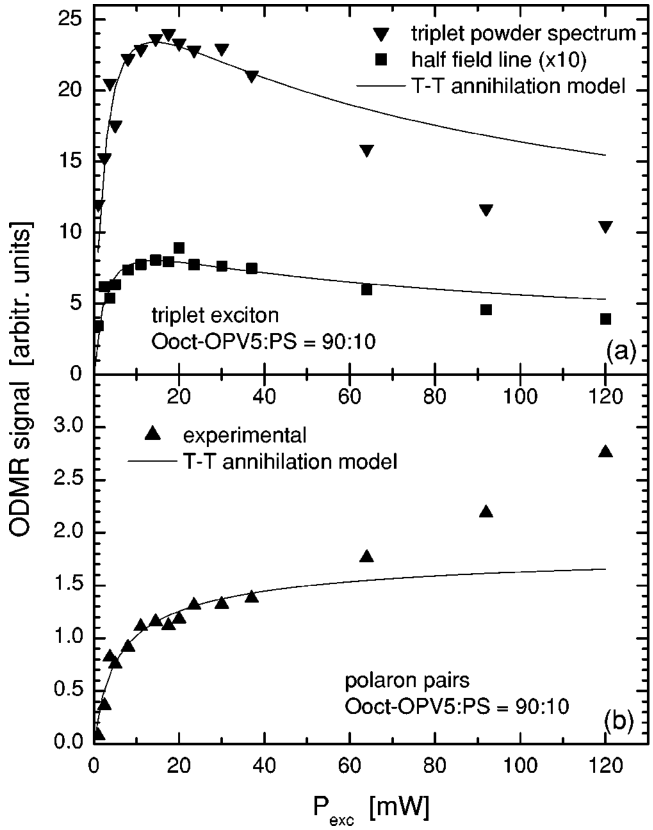

FIG. 5. Dependence of the ODMR intensity on the power of the excitation light for the (30:70) Ooct-OPV5 in the PS sample (a) triplet exciton and (b) polaron pair ($T=2.7$ K, $\lambda_{exc}=476$ nm, and $P_{\mu w}=200$ mW)., compared to the T-T annihilation model, as discussed in the text.

where P_{P-} and P_{P+} are the spin polarizations for negative and positive polarons, respectively.

D. Optical excitation intensity dependence

Figure 5 shows the ODMR intensity of both the TEs and the PPs as a function of the intensity of the incident light for the case of a (90:10) ratio of Ooct-OPV in PS. These experiments were performed for the three different concentration of the Ooct-OPV5:PS blend in order to obtain more information on TE and PP formation rates. The ODMR intensity of each signal was determined as an integrated intensity over a well-chosen interval on the magnetic field axis: the width of the spectrum extended by 5 mT to the left and right of it. The PP intensity was obtained from a limited interval around the narrow line. This amount was also subtracted from the total signal in the wider range around $g=2$ in order to obtain a reliable TE intensity. All results were normalized by dividing the integrated intensities by the number of accumulated spectra and by PL intensity as measured by the photodetector. The PL intensity was found to be near to linear with the optical excitation intensity (not shown) and is higher for films with higher oligomer concentration. For comparison, the ODMR intensity of the half-field ($g\approx 4$) signal is also presented [Fig. 5(a)]. Its excitation intensity dependence is essentially proportional to that of the full field triplet signal ($g\approx 2$), as would be expected.

At low excitation levels, a fast increase of both S_{ODMR}^{TE} and S_{ODMR}^{PP} is observed, which means the modulated signal ΔI_{PL} is increasing faster than the PL intensity I_{PL}. At higher excitation intensities, the PP signal increases further, albeit at a slower pace, whereas the TE signal reaches a maximum and then gradually decreases. These results for oligomers are in qualitative agreement with those obtained for conjugated polymer PPV by Dyakonov and Frankevich,[28] although their experiments hardly reach beyond the region of maximum TE signal. Qualitatively one can explain the observed behavior in the following way: initially there are only a few molecules excited. SEs are created, which contribute to the PL or dissociate into PPs. Furthermore, part of the SE is converted to a TE as a consequence of ISC. The fast initial increase of the ODMR signals indicates that the underlying reactions cannot be first-order processes involving only a TE or only a distant PP. Within the T-T annihilation model described in Ref. 28, a second-order reaction is introduced in which pairs of TEs can interact and annihilate resulting in a SE contributing to the PL with a reaction constant γ depending on the spin states within the TEs. This explains the initial increase of the TE ODMR signal in weak excitation conditions, but also leads to a relative depletion of the TEs when the second order recombination rate is drastically increasing with exciton concentration. Another element in the model is the relaxation of an appreciable part of the triplet PPs into TEs, at a rate p_3 that depends on the spin state of the PP. This TE generation rate is considered to be proportional to the excitation power. The constants γ (of a second order reaction) and p_3 (of a first order one) enter into the rate equations for the system and hence the expression for the delayed PL in different ways, leading to different saturation behaviors for the TE and PP ODMR signals, respectively. The dependence excitation power (proportional to p_3) is given by[28]

$$S_{ODMR}^{PP}\sim\frac{\sqrt{1+4\dfrac{\gamma}{k_T^2}p_3}-1}{\sqrt{1+4\dfrac{\gamma}{k_T^2}p_3}},$$

$$S_{ODMR}^{TE}\sim\frac{\sqrt{1+4\dfrac{\gamma}{k_T^2}p_3}-1}{\sqrt{1+4\dfrac{\gamma}{k_T^2}p_3}\left(\sqrt{1+4\dfrac{\gamma}{k_T^2}p_3}+1\right)},$$

in which k_T is the rate constant for (non-radiative) recombination of the TEs.

Figure 5 shows simulations for the TE and PP ODMR intensities (S_{ODMR}^{TE} and S_{ODMR}^{PP}, respectively) based on this derivation, taking $4\gamma/k_T^2p_3=bP$ proportional to the excitation power P. The simulations were fitted on the data points

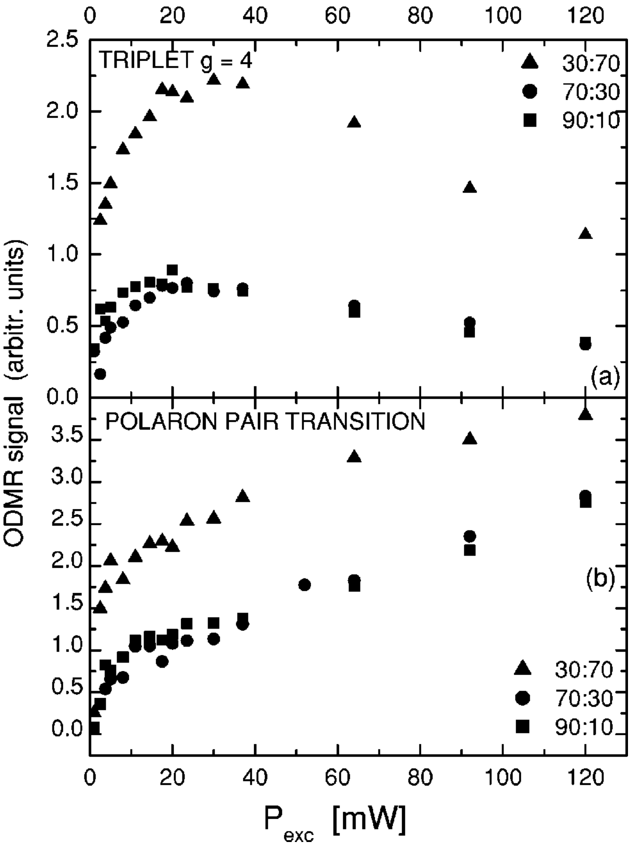

FIG. 6. Dependence of the ODMR intensity on the power of the excitation light for the three oligomer concentrations, (a) for the triplet g=4 transition, (b) and for the polaron pair transition. ($T=2.7$ K, $\lambda_{exc}=476$ nm, and $P_{\mu w}=200$ mW).

below $P=50$ mW, omitting the last three data points. This yields a reasonable agreement in this range, using the same proportionality constant b within a set of data taken on a given oligomer/PS composition which could be measured in a continuous experimental run. The following parameter values were derived from the data in Figs. 5 and 6: $b=0.34$ mW^{-1} for the composition (90:10), 0.11 mW^{-1} for (70:30), and 0.3 mW^{-1} for (30:70). It is not straightforward to relate this values to the physical constants of the model because of the difficulty of calibration of the power density on the sample, and the lack of knowledge of the different rate constants involved.

At higher excitation powers the experimental data strongly deviate from the model, that is seen to underestimate both the rate of decrease of the TE signal and the rate of increase of the PP signal in this region (see Fig. 5). However, one should consider that the above derivation is valid only for a strongly simplified case of the T-T annihilation model: The rate constant γ for annihilation is taken to be the same for all pairs of TEs, regardless of the relative position of the oligomers on which they are located. In particular, an increase of this constant is expected for decreasing distance between TEs, which is on average the case for higher TE concentrations occurring at higher excitation power. Several other possible extensions of the model may be envisaged: (i) In the rate equations, only TE formation via triplet PP decay is considered, and eventually direct ISC from SE to TE should be included. (ii) The effect of the different spin statistics which result for recombination of geminate vs nongeminate PPs. In the first case they are expected to stay mainly in the singlet state since they originate from dissociation of a SE, while 25% singlet and 75% triplet yields are expected as a result of a pure statistical distribution in the second case. The relative amount of nongeminate PPs, especially those in a triplet spin state, will drastically increase with the PP concentration, i.e., in the high excitation regime. (iii) Finally, one could question the assumption that only annihilation between pairs of TEs leads to an ODMR signal (and that the only mechanism by which PPs enter the ODMR process is decay of PP into a TE). It is not excluded that at high powers other second-order interactions come into play such as between a TE and a triplet PP, which could become a singlet PP and recombine to a SE, or alternatively could lead to an annihilation reaction forming a SE. Such additional pathways could also resolve the question of the shorter response time for the PP ODMR signal compared to that of the TEs (Sec. III. C), which cannot be explained by the assumed spin dependence of the rate constant for decay of the triplet PP into a TE. However, the basic elements of the T-T annihilation model can be reconciled with the measured response times if one considers that the spin state is preferentially conserved in the triplet PP to TE relaxation. If such a spin memory effect is assumed, the different response times observed for the ODMR signals could be identified as the lifetimes of the TE$_0$, and the TE$_{\pm 1}$ states (TE states with a quantum number of the spin projection of $M=0,\pm 1$). The available data are unfortunately insufficient to decide which of the refinements of the models is most important.

E. Effects of oligomer concentration

The power excitation dependence was determined for different concentrations of the pentamer in PS, as shown in Fig. 6. It is clear that the films with the lowest concentration (30:70 ratio for Ooct-PPV:PS) yield a much higher ODMR signal, overall, than the two highly concentrated ones (70:30 and 90:10). In this respect the latter two concentrations seem to behave similarly, and represent the limit in which an oligomer is nearly completely surrounded by other oligomer neighbors.

One might have expected the opposite result: A higher concentration means more TEs, closer to one another. The optical density of the films is proportional to the oligomer concentration within the uncertainties on film thickness. Hence, the T-T annihilation process would occur with a higher probability and the contribution of TEs to the spectrum would be relatively larger for films with a higher concentration. For the PPs essentially the same effect is expected. A higher concentration of molecules and possibly a higher degree of aggregation would enhance SE dissociation into PPs. As a consequence, more PPs should be observed with ODMR. Moreover, nongeminate recombination of PPs into TEs would also occur at a higher yield. But experimentally, the TE signal in more concentrated films is smaller than at lower concentrations.

The following suggestion is made to explain the results. The T-T annihilation model, as applied for the fitting of the excitation power dependence, only takes into account TE formation via nongeminate PP recombination. Although the experimental results shows anomalies at higher powers, the overall behavior is in accordance with the model. In films of higher concentrations, the probability for SEs to dissociate into PPs becomes higher, as is the nongeminate recombination of PPs into TEs. Moreover, since the film has a higher density, the T-T annihilation rate will be higher, which would show itself in an increasing ODMR signal. Since the opposite is observed, another decay process must compete with the creation rate p_3 and the annihilation rate γ, most probably the first-order decay described by the rate constant k_T. Due to the higher density of molecules in the film, the nonradiative decay of TEs becomes more important. This is why TEs and also PPs, which are detected via the annihilation of the intermediate TE state, are less observed in the ODMR spectra. Since the T-T annihilation model gives a good description of the excitation power dependence, we expect that direct TE formation via ISC is not important, but that it may have a higher probability in films with lower concentrations with a larger fraction of ‘‘isolated’’ molecules.

IV. CONCLUSIONS

In this work, a series of ODMR measurements of spin coated films of Ooct-OPV5, a substituted oligo(*para*-phenylenevinylene), were presented. The analysis of the triplet powder ODMR spectrum at $g=2$, together with the $g\approx 4$ line, showed that the zfs tensor has, within experimental accuracy, an orthorhombic zero-field splitting, with values $D\approx 0$ and $E=0.037\pm 0.002\ \mathrm{cm}^{-1}$. The symmetry and ODMR line shape suggest that the TE is localized mainly on the octyloxy substituted phenyl unit. We report on the excitation power dependence of the ODMR intensities on films of these oligomer/PS blends, comparable to previous results on PPV polymers,[28] but measured in a wider range. Our results essentially confirm the validity of the T-T annihilation model in this oligomer/PS system, but refinement is necessary. Indeed, at higher powers the experimental curves deviate from the simple model, and a significantly shorter response time is found for the PP signal compared to that of the TEs. Possible origins of these discrepancies are (i) an increase of T-T annihilation rate constant at higher TE concentrations, (ii) the neglect of the direct ISC from SE to TE, (iii) the possible existence of additional annihilation pathways (e.g., by interactions between a TE and a triplet PP), (iv) neglect of the different spin statistics for geminate and nongeminate recombinations (at low and high excitation powers, respectively), and (v) the spin memory effect in the relaxation from triplet PP to TE states. The decreasing ODMR signal in films with higher oligomer concentration is ascribed to an increasing nonradiative TE decay rate in larger molecular aggregates.

ACKNOWLEDGEMENTS

The authors thank J. Wildeman and G. Hazíioannou from the University of Groningen who prepared and provided the oligomer compound. We wish to acknowledge the help of W. Geens in spincoating of *X*-band samples. This work is supported by the Fund for Scientific Research, Flandres (FWO). The Laboratory for Experimental Condensed Matter Physics (ECM) of the University of Antwerp acknowledges financial support from the Flemish Government in the GOA concerted action Multi-disciplinary Spectroscopic Investigation of Organic Materials and Biomolecules (99/3/34). V.D. gratefully acknowledges financial support by German Research Council (DFG) (Grant No. PA378/3).

---

[1] L.S. Swanson, P.A. Lane, J. Shinar, and F. Wudl, Phys. Rev. B **44**, 10617 (1991).

[2] Z.V. Vardeny and X. Wei, Mol. Cryst. Liq. Cryst. **256**, 465 (1994).

[3] V. Dyakonov, G. Rösler, M. Schwoerer, and E.L. Frankevich, Phys. Rev. B **56**, 3852 (1997).

[4] R.G. Sun, Y.Z. Wang, D.K. Wang, Q.B. Zheng, E.M. Kyllo, T.L. Gustafson, Fosong Wang, and A.J. Epstein, Synth. Met. **111–112**, 595 (2000).

[5] J. Sujatha and A.K. Mishra, J. Photochem. Photobiol., A **101 (2–3)**, 245 (1996).

[6] S.C. Graham, D.D.C. Bradley, and R. H. Friend, Synth. Met. **41**, 1277 (1991).

[7] D. Beljonne, J. Cornil, J.L. Bredas, and R.H. Friend, Synth. Met. **76**, 61 (1996).

[8] Y. V. Romanovskii, A. Gerhard, B. Schweitzer, R.I. Personov, and H. Bässler, Chem. Phys. **249**, 29 (1999).

[9] J. Partee, E.L. Frankevich, B. Uhlhorn, J. Shinar, Y. Ding, and T.J. Barton, Phys. Rev. Lett. **82**, 3673 (1999).

[10] E.L. Frankevich, A.A. Lymarev, I. Sokolik, F.E. Karasz, S. Blumstengel, R.H. Baughman, and H.H. Hörhold, Phys. Rev. B **46**, 9320 (1992).

[11] *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model*, edited by N.S. Sariciftci, (World Scientific, Singapore, 1997).

[12] J.W.P. Hsu, M. Yan, T. M. Jedju, L.J. Rothberg, and B.R. Hsieh, Phys. Rev. B **49**, 712 (1994).

[13] J.G. Müller, U. Lemmer, J. Feldmann, and U. Scherf, Phys. Rev. Lett. **88**, 147401 (2002).

[14] K. Murata, Y. Shimoi, S. Abe, S. Kuroda, T. Noguchi, and T. Ohnishi, Chem. Phys. **227**, 191 (1998).

[15] J. Shinar, in *Handbook of Organic Conductive Molecules and Polymers: Vol 3. Conductive Polymers: Spectroscopy and Physical Properties*, edited by H.S. Nalwa, (Wiley, New York, 1997), pp. 320–366.

[16] V. Dyakonov, in *Primary Photoexcitations in Conjugated Polymers* (Ref. 11), Chap. 10.

[17] P. A. Lane, X. Wei and Z. V. Vardeny, in *Primary Photoexcitations in Conjugated Polymers* (Ref. 11), Chap. 11.

[18] L.S. Swanson, J. Shinar, and K. Yoshino, Phys. Rev. Lett. **65**, 1140 (1990).

[19] C.J. Brabec, V. Dyakonov, N.S. Sariciftci, W. Graupner, G. Leising, and J.C. Hummelen, J. Chem. Phys. **109**, 1185 (1998).

[20] J.H. Burroughes, D.D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, and A.B. Holms, Nature (London) **347**, 539 (1990).

[21] R.H. Friend, J. Burroughes, and T. Shimoda, Phys. World **12**, 35 (1999).

[22] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R. N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J. L. Bredas, M. Löglund, and W.R. Salaneck, Nature (London) **397**, 121 (1999).

[23] J. Kido, Phys. World **12**, 27 (1999).

[24] J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Köhler, and R.H. Friend, Nature (London) **413**, 828 (2001).

[25] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, and S.R. Forrest, Nature (London) **395**, 151 (1998).

[26] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, and S.R. Forrest, Appl. Phys. Lett. **75**, 4 (1999).

[27] R.E. Gill, A. Meetsma, and G. Hadziioannou, Adv. Mater. **8 (3)**, 212 (1996).

[28] V. Dyakonov and E. Frankevich, Chem. Phys. **227**, 203 (1998).

[29] The $D=0$ case is equivalent to the case $E=\pm D/3$ for a different labeling of the x, y, and z local axes. The alternative identification of the triplet spectrum is an axial system ($E=0$, $D\approx 0.1\ \mathrm{cm}^{-1}$), in which the symmetrical features around $g=2$ would correspond to the perpendicular contributions in the powder EPR spectrum, while parallel contributions would be unobservable because of vanishing ODMR efficiencies. This, however, leads to a half-field at too low fields by more than 7 mT, well outside of the linewidth (3 mT) and experimental uncertainties.

[30] T. Barhoumi, S. Romdhane, A. Ben Fredj, F. Kouki, and H. Bouchriha, Synth. Met. **130**, 111 (2002).

[31] C. Brabec, F. Padinger, N. Sariciftci, and J. Hummelen, J. Appl. Phys. **85**, 6866 (1999).

[32] A.R. Brown, K. Pichler, N. C. Greenham, D.D.C. Bradley, R.H. Friend, and A.B. Holmes, Chem. Phys. Lett. **210**, 61 (1993).