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Photophysics of a poly(phenylenevinylene) with alternating *meta*-phenylene and *para*-phenylene rings

P. A. Lane, A. J. Cadby, H. Mellor, S. J. Martin, D. G. Lidzey, and D. D. C. Bradley
Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom

S. M. Lipson, D. F. O'Brien, and W. J. Blau
Department of Physics, Trinity College, University of Dublin, Dublin 2, Ireland

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We have investigated the photophysics of the luminescent polymer poly(1,3-phenylenevinylene-*alt*-2,5-dioctyloxy-1,4-phenylenevinylene) by a variety of optical spectroscopies. The incorporation of alternating *meta*-phenylene and *para*-phenylene rings restricts conjugation with respect to poly(*para*-phenylenevinylene) derivatives. As a consequence, excited states are blueshifted and the nonlinear susceptibility is reduced. Absorption by aggregates, which can be obscured by scattering and interference, is clearly revealed by electroabsorption spectroscopy. The reduced symmetry of 1,3-PPV modifies optical selection rules, resulting in strong overlap of the fluorescence spectrum with excited state absorption by charged polarons.

I. INTRODUCTION

Conjugated polymers have been successfully utilized as the emissive layers in organic light emitting diodes (LEDs) over the last decade. Poly(*para*-phenylenevinylene) (PPV) has been intensively studied and many chemically substituted derivatives of this conjugated polymer have been synthesized. One path that has been pursued to enhance the PL efficiency of conjugated polymers is to develop polymers with lower conjugation lengths so to hinder exciton migration to quenching sites.[1] Introducing *meta*-phenylene rings into the polymer chain is one way to restrict conjugation.[2–4] Studies of PPV derivatives with alternate *meta*- and *para*-phenylene rings, have shown that the absorption and emission spectra are blueshifted relative to PPV.[5–7] This should restrict exciton diffusion to quenching sites and lead to increased PL quantum efficiency.

Such polymers also provide a valuable testing ground to explore the interplay between the molecular symmetry and electronic states. PPV has C_{2h} symmetry and its electronic states are labeled A_g or B_u. The corresponding symmetry labels of molecular orbitals are a_g and b_u. For transitions between states and orbitals, dipole selection rules require that the levels have opposite parity. In contrast, C_{2h} symmetry will be broken by the inclusion of *meta*-phenylene rings. A further modification of the PPV electronic structure arises from different contributions of the six phenylene molecular orbitals to the delocalized π-electron system. Only the pair of orbitals polarized along the axis of the phenylene ring parallel to the polymer chain contribute to the delocalized π-electron system of PPV.[8] There is no such preferential orientation of the *meta*-phenylene ring, which will alter the contribution of phenylene molecular orbitals to the delocalized π-electron system. The prospect of device applications and novel photophysics motivates a detailed study of the photophysics of 1,3-PPV.

The outline of this paper is as follows. In Sec. II we describe the experimental techniques used in this work and explain how spectra are interpreted. The chemical analysis of 1,3-PPV is also briefly discussed. Absorption and electroabsorption measurements of 1,3-PPV films are discussed in Sec. III. We show that the inclusion of a *meta*-phenylene ring restricts π-conjugation and alters the symmetry of electronic states. As a consequence, there is no evidence for field-induced absorption by the mA_g state seen in other PPV derivatives. Evidence for aggregation within 1,3-PPV films is also presented. Measurements of photoexcitation dynamics and photogeneration mechanisms are discussed in Sec. IV. The reduced symmetry of 1,3-PPV results in an additional allowed absorption band for polarons not seen for *para*-phenylene derivatives of PPV. This blueshifts polaron absorption to the peak of the fluorescence spectrum, resulting in reduced PL yields and quenching of laser action. We then summarize our results and conclude.

II. EXPERIMENTAL METHOD

Poly(1,3-phenylenevinylene-*alt*-2,5-dioctyloxy-1,4-phenylenevinylene) was synthesized by the Wittig reaction, a reaction between Wittig salts and isophthalic dialdehyde.[9] We refer to this polymer as 1,3-PPV and show the structure in the upper right-hand corner of Fig. 1. 1,3-PPV has been fully characterized via a variety of analyses and we report here only the outline details. Further details are given elsewhere.[5,10] Gas phase chromatography measurements with polystyrene as the calibration standard show a typical relative number average molecular weight of $M_n = 15\,200$ (35 repeat units containing 70 phenylene rings) and a polydispersity of 2.5. The results of the ^{1}H and ^{13}C nuclear magnetic resonance measurements in deuterated chloroform indicate that the polymer structure is as proposed and that the resulting configuration of the vinylene unit is a mixture of *cis* and *trans*, with the majority in the *trans* configuration. The polymer infrared spectrum also shows the expected features.[11] The maximum PL quantum efficiency in solutions reaches 82% in dioxane with some batch-to-batch variation. Lowest efficiencies in a variety of solvents are between 65%

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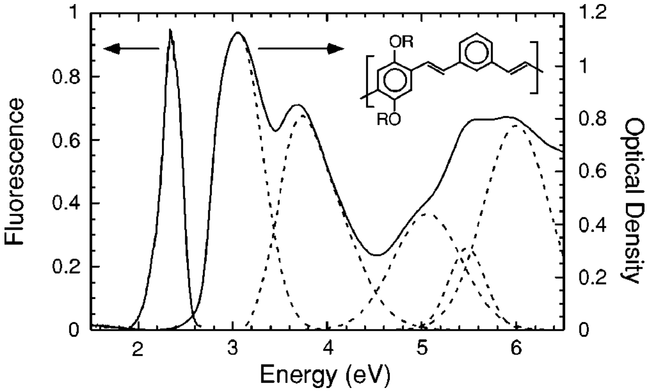

FIG. 1. The absorption (solid line, right axis) and fluorescence spectra (solid line, left axis) of 1,3-PPV. The dashed lines show the individual absorption bands. The co-polymer repeat unit is shown in the inset.

and 70%. These values were obtained using a calibrated integrating sphere and have been confirmed by separate measurements undertaken at the University of Regensburg.[6] 1,3-PPV shows the desired high PL efficiency for which it was designed. Lasing is readily achieved for 1,3-PPV in solution under pulsed excitation. The characteristics of the laser action are described in detail elsewhere.[6]

The absorption and fluorescence spectra were measured with calibrated spectrophotometers. The electronic structure of 1,3-PPV was also studied by electroabsorption (EA) spectroscopy. In an EA experiment, a sinusoidal electric field modulates the absorption of light. For nondegenerate states and to second order in the applied electric field, the change in the optical absorption is proportional to a combination of the first and second derivatives of the absorption coefficient with respect to energy. These arise from differences in the polarizability ($\partial\alpha/\partial E$) and/or permanent dipole moment ($\partial\alpha^2/\partial E^2$) of the ground and excited states.[12] The electric field also mixes the symmetry of electronic states, which causes a transfer of oscillator strength from allowed to forbidden optical transitions. This results in bleaching of the allowed absorption and the appearance of induced absorption bands in the EA spectrum.[13–19] Samples were mounted in a cold-finger liquid nitrogen cryostat equipped with optical and electrical access. A sinusoidal electric field modulated at 5 kHz was applied to the sample using the reference output of a lock-in amplifier driving a high voltage amplifier. Light is dispersed through a monochromator, focused onto the sample and then is detected by a silicon photodiode. Lock-in amplification was employed to detect changes, ΔT, in the transmission T.

Photoexcitation dynamics were studied by photoinduced absorption (PA) spectroscopy. For PA measurements, the sample is excited by an amplitude-modulated pump beam and changes in the transmission of a probe beam are measured by lock-in amplification of a photodetector. The 457.9 nm line of an argon ion laser at a power density of 30 mW/cm^2 was used as the pump beam and a monochromated tungsten white light source was used as the probe. The use of multiple detectors and gratings enabled the PA spectrum to be investigated between 0.7 and 3.0 eV. The pump beam was modulated at 120 Hz by an acousto-optical modulator and the spectra were measured under vacuum at 80 K. The PA spectrum, defined as the normalized change, ΔT, in transmission of the probe beam, T, is proportional to the photoexcitation density, n. This in turn is proportional to the product of the excited state lifetime and the quantum yield η:

$$-\Delta T/T = n\sigma d = \eta S\sigma\tau, \tag{1}$$

where σ is the excited state crosssection, S is the pump density (photons per unit area), and τ is the excitation lifetime. The lock-in amplifier simultaneously measures the in-phase and quadrature signals, which can be compared to determine the excitation lifetime and correlate different PA bands. For monomolecular recombination, the in-phase and quadrature PA signals will, respectively, depend upon the modulation frequency ($f=\omega/2\pi$) and the excitation lifetime τ as[20]

$$\Delta T_{\mathrm{IN}} \propto 1/[1+(\omega\tau)^2], \tag{2}$$

$$\Delta T_{\mathrm{QUAD}} \propto \omega\tau/[1+(\omega\tau)^2]. \tag{3}$$

III. ELECTRONIC STRUCTURE OF 1,3-PPV

The absorption and fluorescence spectra of a 1,3-PPV film are shown in Fig. 1. The absorption edge is at 2.65 eV with maxima at 3.05 and 3.69 eV. There are also absorption bands at 4.9, 5.5, and 6.0 eV. The dashed lines in Fig. 1 show a deconvolution of the absorption bands, assuming Gaussian tails. The optical gap of 1,3-PPV is blueshifted by 0.34 eV with respect to that of DOO–PPV. The width of the observed absorption features is due to both unresolved vibronic structure and inhomogeneous broadening. The absorption spectrum of 1,3-PPV is significantly redshifted from that of distyrylbenzene, for which the lowest energy absorption peak is at 3.48 eV with vibronic features at 3.30 eV, 3.64 eV, and 3.85 eV.[21,22] The PL spectrum of 1,3-PPV peaks at 2.42 eV, with a shoulder present at 2.34 eV. The fluorescence efficiency of a neat film, measured with an integrating sphere and exciting at 354 nm, was measured to be 25±1%. This compares favorably to a previous study by Holzer *et al.*, where the PL efficiency of a 1,3-PPV solution was measured to be 64%, but that of a neat film to be only 4.7%.[6] Pang *et al.* have reported solid state fluorescence efficiencies between 61% and 82% for the hexyloxy and butyloxy equivalents of 1,3-PPV.[7] However, these measurements were performed by comparison to a standard rather than using a calibrated integrating sphere and therefore may not be directly comparable.

The effect of alkoxy substitution on the absorption spectrum of PPV has been widely debated. The absorption spectrum of PPV consists of bands at 3.0, 3.8, 4.8, and 6 eV.[8,23–26] Substituted derivatives of PPV exhibit the same structure, although the energy and relative strength of each band depends upon the substituent. 1,3-PPV shows two significant differences from other substituted PPV derivatives: the absorption band at 3.8 eV (band II) is unusually strong and an additional band at 5.5 eV can be seen. Absorption band II is similarly strong in the 1,3-PPV derivatives synthesized by Pang *et al.*[7] The origin of band II has been controversial. Some workers have assigned this band to a forbidden transition which becomes allowed because of charge conjugation symmetry (CCS) breaking by the sidechains.[23–25]

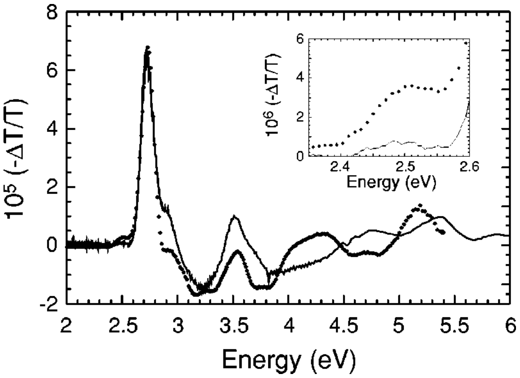

FIG. 2. The electroabsorption spectrum of 1,3-PPV (symbols) and the derivative of the absorption spectrum with respect to energy (line). The inset shows the low-energy portion of the EA spectrum on an expanded scale.

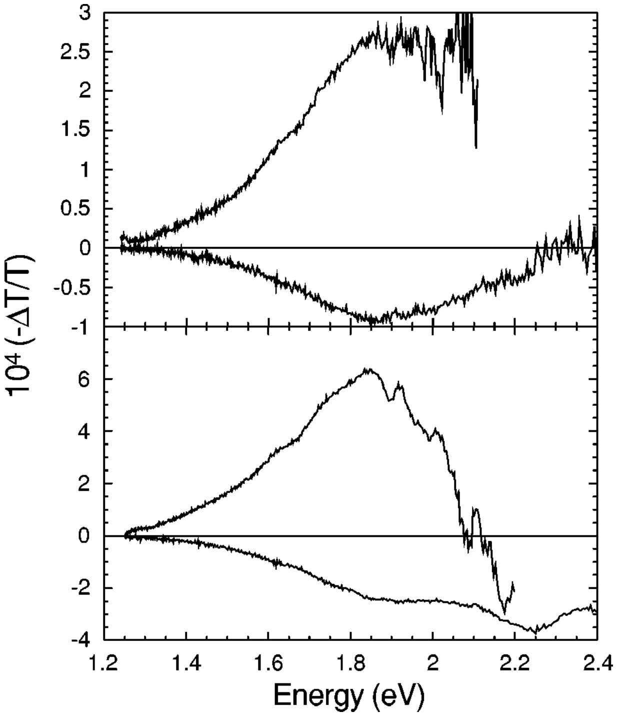

FIG. 3. In-phase (top) and quadrature (bottom) PA spectra of a (a) neat film of 1,3-PPV and (b) a blend containing 60% 1,3-PPV and 40% polystyrene by weight.

Others believe that the effects of CCS breaking alone are weak and have little effect on the optical properties of the material.[8,26–28] Within this context, the strength of band II is closely related to the effective conjugation length of the polymer. It is therefore intriguing that band II is especially strong in 1,3-PPV, where the incorporation of *meta*-phenylene rings alters the symmetry and restricts conjugation.

An essential assumption of many PPV models is that the photophysics of the lowest excited state of the polymer, arising from the six orbitals of a phenylene ring (and the orbitals of the vinylene bond), can be described by two of the phenylene molecular orbitals which are polarized along the long axis of the polymer chain, one of the two degenerate e_{1g} highest occupied molecular orbitals (HOMO) and one of the two degenerate e_{2u} lowest unoccupied molecular orbitals (LUMO). The different absorption bands of PPV derivatives are due to transitions (i) between delocalized ($d \rightarrow d^*$), (ii) and (iii) mixed transitions ($d \rightarrow l^*, l \rightarrow d^*$), and (iv) transitions between localized orbitals ($l \rightarrow l^*$). Conjugation across *meta*-phenylene rings requires inclusion of both pairs of degenerate phenylene molecular orbitals. This could possibly explain the unusual strength of the 3.8 eV and the emergence of an additional peak at 5.5 eV not seen in *para*-phenylene PPV derivatives.

The electroabsorption spectrum and the first derivative of the absorption spectrum with respect to energy are shown in Fig. 2. The main EA peak at 2.73 eV follows the derivative absorption spectrum indicating that a redshift of absorption due to the Stark effect has occurred. Both the EA and derivative spectra contain a vibronic sideband at 2.9 eV and a second peak at 3.5 eV, which is related to the absorption band at 3.64 eV. Above 4 eV, the EA and derivative spectra are not well correlated. The main differences to note between the EA and derivative absorption spectra are the initial feature at the onset of EA at approximately 2.5 eV, an unusual doubling occurring at the minima of the EA spectra, and deviations above 4 eV.

The *meta*-phenylene ring in 1,3-PPV alters the symmetry of the material and restricts π conjugation. The third order nonlinear susceptibility of 1,3-PPV at the EA peak (2.9 eV) was calculated using Kramers Kronig relations. These values were determined to be $\Re\gamma = 1.28 \times 10^{-11}$ esu and $\Im\gamma = 1.73 \times 10^{-11}$ esu. Comparison of the derivative absorption and EA spectra in Fig. 3 results in a maximum polarizability $\Delta p = 623$ Å^3 at 2.9 eV, more than an order of magnitude less than Liess *et al.*[19] calculated for several luminescent conjugated polymers (including substituted PPV derivatives). The polarizability of the lowest excited state of 1,3-PPV is only 50% larger than that of *trans,trans*'-distyrylbenzene (420 Å^3).[24] The much lower polarizability of 1,3-PPV is consistent with restricted conjugation owing to incorporation of *meta*-phenylene rings.

The feature at the onset of the EA spectrum is shown on an expanded scale in the inset of Fig. 2. A clear maximum with $-\Delta T/T = 3.5 \times 10^{-6}$ is seen at 2.5 eV. This feature cannot be due to activation of a symmetry forbidden transition lying below the main absorption band as 1,3-PPV is highly luminescent. As strong fluorescence proceeds from the lowest lying singlet excited state (Kasha's rule), transitions from the lowest excited state must be dipole allowed. The fact that this feature is more prominent in the EA spectrum than the derivative absorption spectrum suggests that this state has a slightly higher polarizability than that of the main absorption band. The absorption spectrum of 1,3-PPV has a tail between 2.3 and 2.7 eV (Fig. 1). The reduced transmission of the film below 2.3 eV could be due to absorption, scattering, interference fringes or a combination of these effects. The EA spectrum shows that this tail is due to absorption rather than other effects. Photothermal deflection spectroscopy is a useful technique for detecting subgap absorption, but can be difficult to apply near the absorption edge due to saturation of the signal. EA spectroscopy is particularly suited to detecting such states as it is insensitive to scattering, but can still be used even when there is strong absorption. We suggest that the low energy state is due to aggregates within the polymer film. Aggregation may result from the structure of the polymer chain. The *meta*-phenylene ring induces a 60° bend between repeat units of the co-polymer which would result in a sixfold (6_1) helical configuration of the polymer chain, with 12 phenylene rings per turn. Further studies of the polymer structure are warranted.

The alkoxy sidechain and *meta* link in the 1,3-PPV mean that the polymer does not have the rotation and inversion symmetry typical for PPV derivatives (C_{2h}). Therefore the usual A_g and B_u labelling of states does not apply to this polymer. However, the EA and derivative absorption spectra deviate at energies above the $\pi - \pi^*$ transition. One difficulty in interpretation arises because the EA spectrum covers different absorption bands, which will have differing nonlinear responses. However, it was not possible to effectively model the higher energy EA spectrum either by including different contributions from the absorption bands or by invoking transfer of oscillator strength to a one-photon forbidden transition.[29,30]

The unusual doubling feature seen at the minima of the electroabsorption spectra must be due to the presence of *meta*-phenylene rings. This feature is not observed in the EA spectra of DOO–PPV and other PPV derivatives containing only *para*-phenylene rings.[19,31] However, we have observed similar features in the EA spectra of distyrylbenzene derivatives where the central *para*-phenylene ring has been replaced by a *meta*-phenylene ring.[32] The EA spectrum is a weighted average of a number of phonons that couple to the electronic transition. It may be that the weighting function is different for *meta*-phenylene compounds than for *para*-phenylene compounds or that the change in the molecular symmetry changes which phonon modes couple to the electronic transition.

IV. PHOTOEXCITATION DYNAMICS AND PHOTOGENERATION MECHANISMS

We now turn to studies of photoexcitation dynamics and photogeneration mechanisms in 1,3-PPV. In particular, we are interested in how changing the symmetry of the polymer repeat unit affects excited state absorption spectra. Figure 3 shows the PA spectra of (a) a neat film of 1,3-PPV and (b) a blend containing 60% 1,3-PPV and 40% polystyrene by weight. The latter film was prepared in order to disrupt aggregation. The absorption and fluorescence spectra of the blended film do not substantially differ from the neat film, though its fluorescence efficiency (29%) is somewhat higher than that of the neat film (25%). The in-phase PA spectra above 2.0 eV are unreliable due to contamination of the PA spectrum by fluorescence. Heating of the sample by the probe beam modulates the magnitude of the fluorescence and thermochromic shifts can make it impossible to correct by simply scaling the PL intensity. However, there was virtually no contribution of fluorescence to the quadrature PA signal. Both samples have a PA band with a maxima at 1.87 eV; the neat film also has a second PA band with a maximum at 2.25 eV.

There are two possible candidates for the PA bands: charged polarons and neutral triplet excitons. Figure 4 shows the absorption spectra of a solution of 1,3-PPV at a concentration of 1.25 g/l in dichloromethane doped by $FeCl_3$ at a concentration of 3.75 g/l (0.023 M). The polymer is oxidized by the dopant and the absorption spectra show the formation of an absorption band with a peak at 2.28 eV (543 nm) due to positive polarons on the polymer chain. The line shape of the doping induced absorption spectrum was independent of the dopant concentration. We did not observe a second oxidation step due to bipolaron (dication) formation. Comparison of the PA spectra shown in Fig. 3 and doping-induced absorption spectrum shown in Fig. 4 lead us to assign the band at 2.25 eV to polarons and the band at 1.87 eV to triplet excitons. The assignment of the feature at 2.25 eV to polarons is supported by comparison of the PA spectra of the two films. In a blend, we observe triplet excitons, but few polarons. From this we conclude that polarons in 1,3-PPV are predominately formed through interchain coupling and disrupting aggregation reduces the polaron population. The reduced PL efficiency with increased charge photogeneration is consistent with quenching of luminescence by polarons through excited state absorption and direct quenching of singlet excitons.

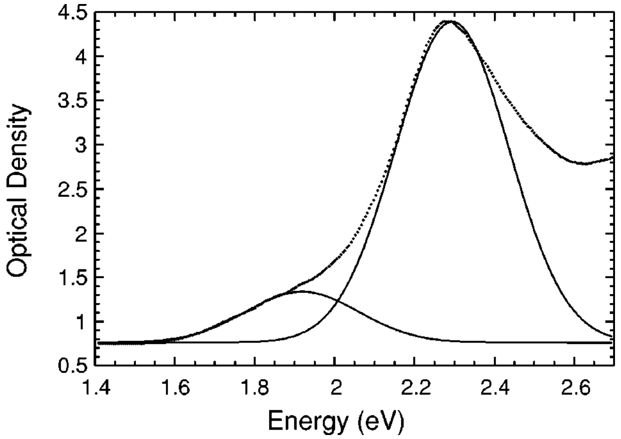

FIG. 4. The absorption spectrum of 1,3-PPV in solution and doped by the addition of $FeCl_3$. The lines show a deconvolution of the polaron absorption into two bands with peaks at 1.92 and 2.30 eV.

The PA spectrum of the neat film consists of overlapping excited state absorption of both polarons and triplet excitons. The relative triplet contribution can be determined by subtracting the polaron absorption (from Fig. 4) from the quadrature PA spectrum of the neat film. Figure 5 compares the triplet absorption of the neat film, scaled by a factor of 2, to the PA spectrum of the blended film. The two spectra are identical with the triplet PA of the neat film twice that of the blended film. The larger triplet PA in the neat film is related to either a change in the excited state lifetime or the quantum yield [Eq. (1)]. Both PA bands in the neat film were approximately linear with the laser power, which means that recombination is monomolecular. The excitation lifetime can therefore be determined by measuring the dependence of the PA signals upon the modulation frequency and modelling the results using Eqs. (2) (in-phase) and (3) (quadrature). Figure 6 shows the modulation frequency dependence of the PA bands at 1.87 eV in both films and 2.25 eV in the neat film. The experimental data are shown as symbols and the fits to Eqs. (2) or (3) are shown as solid lines. The triplet lifetime is measured to be 0.46 ± 0.01 ms for both samples and the po-

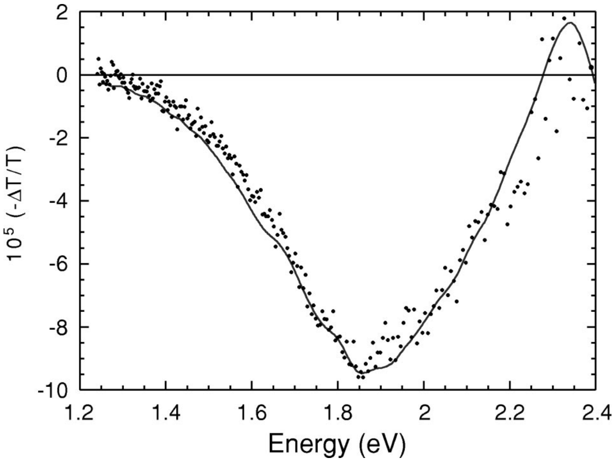

FIG. 5. A comparison of the triplet photoinduced absorption in the blended film (symbols) and neat film (line). The triplet PA spectrum in the neat film was determined by subtracting the polaron absorption (Fig. 4) and scaling by a factor of 2.

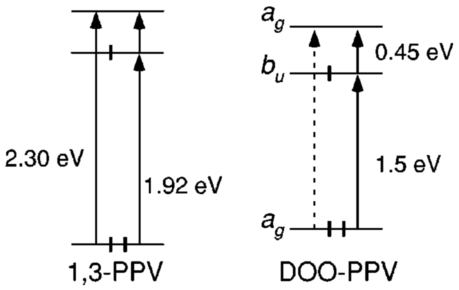

FIG. 7. Schematic diagram of the molecular orbitals of a negatively charged polaron in 1,3-PPV and DOO–PPV. Allowed transitions are shown by solid lines and forbidden transitions by dashed lines.

laron lifetime to be 0.39±0.02 ms for the neat film. There is excellent agreement between the lifetimes calculated using either the in-phase and quadrature signals.

The triplet lifetime is the same in both samples, but the triplet signal of the neat film is twice that of the blended film. As the excitation lifetimes are the same in both samples, the increased PA signal in a neat film is due to a much higher triplet quantum yield [Eq. (1)]. This could be a result of enhanced intersystem crossing or transformation of geminate polaron pairs from singlet to triplet spin configurations before recombination.[33] The latter explanation is consistent with a correlation between enhanced polaron and triplet photogeneration. The excited state absorption peak of triplet excitons occurs at a much higher energy for 1,3-PPV (1.87 eV) than for DOO–PPV (1.45 eV), but at a slightly lower energy than for *trans,trans'*-distyrylbenzene (1.95 eV).[34] This measurement independently confirms the conclusion arising from comparison of the absorption spectra and nonlinear susceptibility of these three materials: incorporation of *meta*-phenylene rings is a useful way in which to engineer the band gap and conjugation length of PPV derivatives.

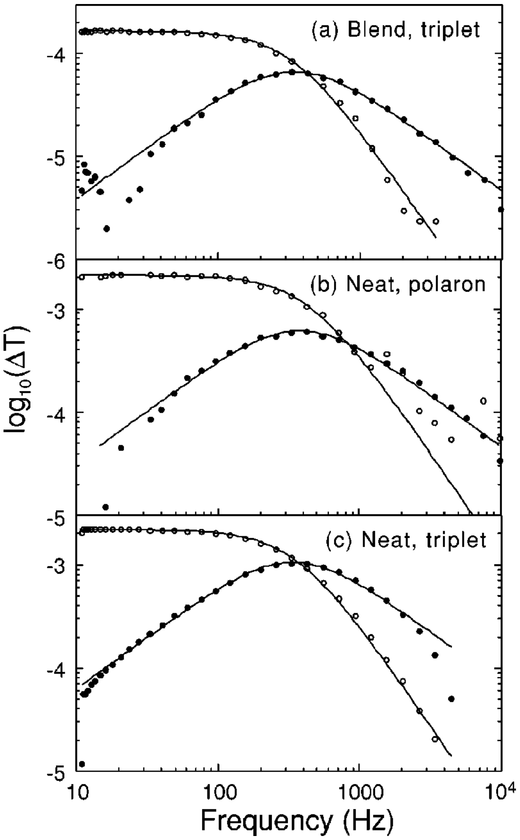

FIG. 6. Dependence of the PA signals upon the modulation frequency. (a) Triplet PA in the matrix isolated film; (b) triplet PA in the neat film; (c) polaron PA in the neat film. In-phase data are shown as filled circles, quadrature data are shown as open circles, and lines are fits to the data using Eqs. (2) or (3).

The excited state absorption spectrum of polarons occurs at a surprisingly high energy and strongly overlaps with the fluorescence spectrum. Whereas the absorption and fluorescence spectra of 1,3-PPV are blueshifted by 0.34 eV with respect to poly(2,5-dioctyloxy-1,4-phenylenevinylene) (DOO–PPV), the absorption peak of polarons is blueshifted by 0.75 eV. This is a consequence of the different symmetries of 1,3-PPV and DOO–PPV. Figure 7 shows a schematic diagram of molecular orbitals for negatively charged polarons in 1,3-PPV and DOO–PPV. The parity of orbitals in DOO–PPV alternates between a_g and b_u, and optical transitions are allowed only between orbitals of opposite parity.[35,36] These selection rules do not hold for corresponding transitions in 1,3-PPV, resulting in a third allowed transition at a relatively much higher energy than for DOO–PPV. The absorption spectra of doped 1,3-PPV in Fig. 4 show a relatively weak band between 1.7 and 1.9 eV, where one would expect to observe polaron absorption. The subgap absorption of doped 1,3-PPV can be resolved into two bands with maxima at 1.92 and 2.30 eV. These are shown as lines in Fig. 4. It is unclear as to why the 2.30 eV peak is much stronger than the 1.92 eV peak.

Although 1,3-PPV readily exhibits lasing in solution[6] and has a high solid state fluorescence efficiency, films of 1,3-PPV did not exhibit spectral narrowing under high intensity excitation seen for other PPV derivatives.[37–39] The lack of spectral narrowing is a consequence of the spectral overlap of the fluorescence and excited state absorption spectra. These results have significant implications in developing new polymers for optoelectronic applications. Developments in recent years have led to the investigation of polymers as suitable materials for an electrically pumped organic laser. The question of whether polymers can be used successfully as a solid state laser material has raised numerous important issues in polymer science: one being excited state absorption by charged species along the polymer backbone.[40] A high density of charge carriers with excited state absorption close to the emission maxima would quench any lasing action and has been highlighted as a major problem in fabricating an electrically pumped organic laser.

V. CONCLUSIONS

In conclusion, we have studied the effect of reduced symmetry on the photophysics of a 1,3-PPV, a PPV derivative with alternating *para*-phenylene and *meta*-phenylene rings. The incorporation of *meta*-phenylene rings restricts π conjugation and alters the symmetry of the polymer with respect to PPVs with all *para*-phenylene rings. As a consequence, the absorption and emission spectra are blueshifted, excited state polarizabilities are reduced and optical selection rules are modified. Studies comparing neat and blended films lead us to conclude that aggregation resulting in interchain coupling is the primary mechanism for charge photogeneration. The blueshifted excited state absorption spectrum of charged polarons effectively quenches laser action in neat films of 1,3-PPV.

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