Optical studies of triplet excitations in poly(*p*-phenylene vinylene)

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We have studied energy states in the triplet manifold in films of poly(*p*-phenylene vinylene) (PPV) using a multitude of optical spectroscopies including photoinduced absorption, photoluminescence, their optically detected magnetic resonances, as well as their photogeneration action spectra. We found that singlet fission into two triplets with opposite spins is an efficient route for triplet generation in PPV, similar in strength to the intersystem crossing process. From the threshold energy for singlet fission we deduced that the lowest-lying, odd-parity triplet excitonic state, 1^3B_u, is located at 1.55 eV from the ground state, which is about 0.9 eV lower than the lowest-lying, odd-parity singlet state 1^1B_u. [S0163-1829(99)50224-5]

Since the first report of electroluminescence (EL) of the organic semiconductor poly(*p*-phenylene vinylene) (PPV),[1] an understanding of its low-lying electronic states has attracted considerable interest.[2–11] Yet, the magnitude of the electron-electron (*e*-*e*) interaction and its role in determining the excited state energies and photoexcitation properties in PPV is, however still unsettled.[6–13] In any case, the observation of EL and its high efficiency implies that there is a one-photon transition from the lowest singlet excitonic state to the ground state where the exciton binding energy is substantially large compared to k_BT. Because these excitons are relatively tightly bound, the spin configuration of the spin-1/2 electron and spin-1/2 hole influences the binding energy, with the spin-triplet lower in energy than the spin-singlet by the exchange energy. The energy separation, Δ_{ST}, between the lowest-lying singlet and triplet excitons may therefore provide one experimental method of measuring the magnitude of the *e*-*e* interaction in PPV.

Since PPV is centrosymmetric (Fig. 1, inset) and thus possesses a C_2 symmetry, its electronic states are divided between odd (B_u) and even (A_g) parity symmetry. Among them the four essential singlet states,[13] which determine the photoluminescence (PL) efficiency and various optical nonlinear spectra are: the ground state, $1A_g$; the first excited B_u state, $1B_u$; an important A_g state, mA_g with strong coupling to the $1B_u$; and the continuum-band threshold, nB_u. The energy levels of the corresponding triplet states, namely 1^3B_u and m^3A_g are not easy to experimentally determine since they are optically forbidden due to the spin selection rule. We note that so far in the field of π-conjugated polymers $E(1^3B_u)$ was only measured in polydiacetylene derivatives[14,15] and polythiophene.[16]

In this work we have studied the most important states in the triplet manifold of PPV, using a variety of c.w. techniques. We found that 1^3B_u is tightly bound with $E(1^3B_u) = 1.55$ eV. Since $E(1^1B_u) \simeq 2.45$ eV we are able to determine Δ_{ST} to be 0.9 eV; this is a large value indicating that electron correlation in PPV is quite strong. Our findings are in agreement with several recent calculations of the excited electronic states in PPV using the Pariser-Parr-Pople (PPP)

model,[8–10] where electron correlation was explicitly taken into account, as well as with a recent *ab initio* calculation.[17]

For the photoinduced absorption (PA) spectroscopy we used a standard photo-modulation setup[18] with a modulated Ar$^+$ laser beam as a pump and several incandescent light sources as a probe, covering the spectral range $\hbar\omega$ from 0.1 to 3 eV. Photoinduced changes ΔT in the sample transmission T were recorded with phase-sensitive techniques to obtain the normalized changes in transmission. We define PA as $\Delta\alpha d = -\Delta T/T = n\sigma d$, where n is the photoexcitation density, σ is the absorption cross section, $\Delta\alpha$ is the absorption change, and d is the sample thickness.

For PA detected magnetic resonance,[18] (PADMR) the sample was mounted in a high Q microwave cavity at 3 GHz equipped with a superconducting magnet and illuminated by the pump and probe beams. We measured the H-PADMR spectrum, in which δT is measured at a fixed probe wavelength λ as the magnetic field H is varied. The action spectrum of PL and PA were measured using as a pump a 250-W Xe lamp through a monochromator, with proper filters and gratings spanning the spectral range E from 1.5 to 4.5 eV. We measured the quantum yield, QY per absorbed photon, where ΔT (or PL) was normalized by the factor $g(E) = RI(E)\{1-\exp[\alpha(E)d]\}$ where $\alpha(R)$ is the film absorption (reflectivity) spectrum and I is the pump intensity spectrum.
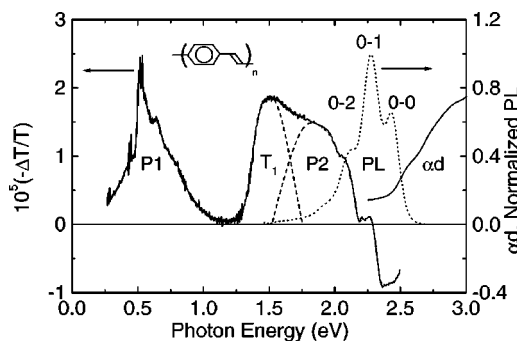

FIG. 1. The photomodulation spectrum of a PPV film at 80 K; the PA bands P_1, P_2, and T_1 are assigned. The PL spectrum and the absorption onset are also shown for comparison. The inset shows the PPV repeat unit.
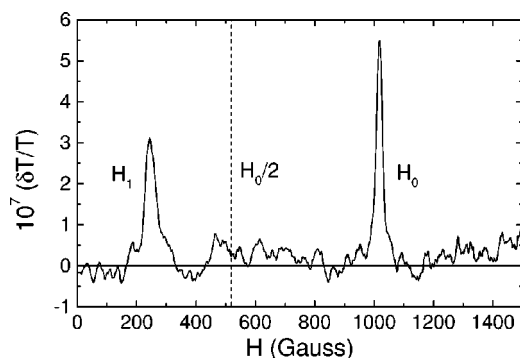
FIG. 2. The H-PADMR spectrum of PPV at $\hbar\omega = 1.5$ eV. The two $\delta T > 0$ resonances at $H_0(s=1/2)$ and at $H_1 < H_0/2$ ($s=1$, "half-field") are assigned.
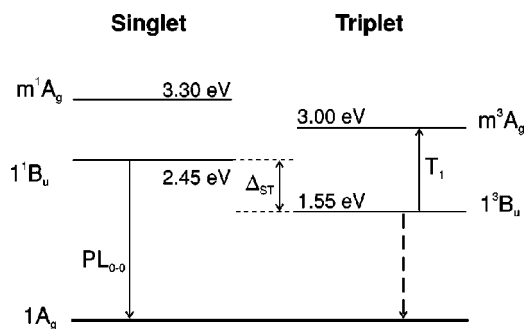

FIG. 3. Energy levels and optical transitions of the most important lowest-lying states in PPV in both singlet and triplet manifolds. The zero phonon emission bands PL_{0-0}, and the T_1 PA transition are also shown.

The PL QY was also normalized at 3.5 eV by the absolute PL QY, η_{PL}, measured by an integrating sphere.

The PPV polymer was synthesized by the commonly used precursor route,[19] where a nonconjugated soluble polymer is cast into films, and then converted to the desired polymer by heating in flowing nitrogen at 220 °C for at least 2 h. After correcting for the optical constants of the integrating sphere in the UV spectral range, we found for our PPV films $\eta_{PL} \simeq 33\%$. This is a high PL QY indicating the high quality of our films.[20]

The photomodulation spectrum of a PPV film on sapphire substrate at 80 K is shown in Fig. 1. As previously reported,[2] the spectrum is composed of two main PA bands, where the higher energy band can be decomposed into two independent PA bands (as shown in Fig. 1) based on their different frequency and temperature dependencies.[2] The strong PL band and its phonon replica, and the absorption onset are also shown in Fig. 1 for comparison. Based on their identical frequency, temperature, and intensity dependencies, the two PA bands at 0.5 (P_1) and 1.8 eV (P_2) are correlated, whereas the band T_1 at 1.5 eV is not correlated with the other two bands.

The H-PADMR spectrum measured at $\hbar\omega = 1.5$ eV is shown in Fig. 2. It contains two $\delta T > 0$ resonance bands; one at $H_0 = 1008$ G ($g \simeq 2$, $s=1/2$ excitations) and the other at $H_1 = 260$ G ($g \simeq 4$, half-field resonance of $s=1$ excitations). To separate these excitations we measured the H-PADMR spectrum at individually selected λ following the various PA bands in the photomodulation spectrum (Fig. 1). From these spectra we could conclude that P_1 and P_2 PA bands are correlated with spin-1/2 excitations, whereas the T_1 PA band is correlated with spin triplet excitations. We therefore identify the P_1 and P_2 bands as the two allowed transitions of long-lived polaron excitations (charge $\pm e$, $s = 1/2$),[21] whereas T_1 is a transition in the triplet manifold, related to long-lived triplet excitations (charge neutral, $s = 1$).[22] Recent model calculations show[9,10] that the most strongly coupled excited state to the 1^3B_u, in the triplet manifold is the m^3A_g. We therefore identify T_1 at 1.5 eV with the transition $1^3B_u \rightarrow m^3A_g$, as shown in Fig. 3.

The wave function extent of the lowest-lying triplet exciton may be obtained from the half-field triplet powder pattern at H_1. This resonance is shifted from $1/2H_0$ due to the zero-field splitting parameters D and E in the Zeeman spin Hamiltonian.[23] If we assume an axial symmetric wave func-

tion, (i.e., $E=0$) we obtain from $H_1 = 260$ G and $D = (H_0^2 - 4H_1^2)^{1/2}$, $D = 864$ G. A useful approximation for the triplet wave-function extension, R is derived[23] where $R^3 = 2.78 \times 10^4/D$; the measured D then gives $R = 3.2$ Å. This shows that the lowest-lying triplet in PPV is highly localized and may be treated as a molecular Frenkel-type exciton. This is in contrast to the singlet $1B_u$ state, which was shown[4] to extend in PPV over about six repeat units. The strong triplet localization found here also shows that the triplet energy level in PPV may be deep inside the optical gap, consistent with a large singlet-triplet energy splitting.

The PL QY spectrum measured with a band pass filter at 2.3 eV is shown in Fig. 4, inset. It shows a step function increase at the optical gap ($\simeq 1^1B_u$) at $E = 2.5$ eV, followed by a flat response up to $E = 4.5$ eV. The flat QY action spectrum has been traditionally associated with excellent polymer film quality,[24] consistent with the high QY ($\eta_{PL} \approx 33\%$) and the weakness of the PA response in our film (Fig. 1).

In Fig. 4 we also show the triplet photogeneration QY action spectrum per absorbed photon using the T_1 PA excitation spectrum. In contrast to the PL QY action spectrum, T_1 QY spectrum is composed of two steps, showing that two different photogeneration channels are operative for the triplet photoproduction in PPV. One process starts at the optical gap and has a flat response similar to that of the PL QY spectrum. We therefore identify this process as mainly due to thermalized excitons, consistent with intersystem crossing (ISC) from excitons at the bottom of the lowest lying excitonic states.[22] We note that the triplet QY spectrum near the onset energy of $E \approx 2.5$ eV is not as sharp as that of the PL QY spectrum, indicating that triplet production is more efficient at higher energies, up to $E \simeq 3$ eV. This is due to a smaller singlet/triplet splitting for more delocalized states, which naturally occurs at higher energies.

The second operative triplet photogeneration process with an onset at $E \simeq 3.1$ eV (Fig. 4) is due to unthermalized excitons. We identify this process as singlet fission (SF),[15] where a singlet exciton (Ex) decomposes into a pair of triplets with opposite spins: $Ex \rightarrow T_\uparrow + T_\downarrow$. The energy barrier for such a process is given by $E > 2E_T$, where E_T is the triplet energy, $E_T = E(1^3B_u)$. Then from the energy onset of the SF process at 3.1 eV we estimate $E_T \simeq 1.55$ eV (Fig. 3). We again note that the triplet QY keeps increasing for $E > 2E_T$, much more than the spectral step related to the ISC
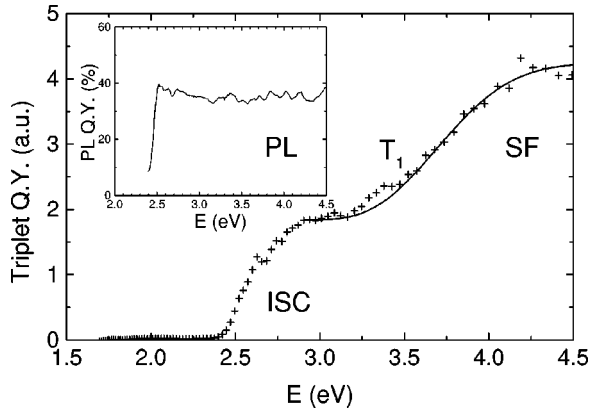
FIG. 4. The triplet QY action spectrum as deduced from the T_1 PA excitation spectrum. Two photogenerated processes, namely intersystem crossing (ISC) and singlet fission (SF) are assigned. The inset shows the PL QY action spectrum, normalized to $\eta_{PL} \simeq 33\%$ measured at $E = 3.5$ eV using an integrating sphere.

FIG. 5. Electroabsorption spectrum in PPV (dashed line) obtained with $F \simeq 10^5$ V/cm. The solid line is the best fit to the summation over states model (Ref. 27) shown schematically in the lower inset. The chain-length distribution used in the calculation is shown in the upper inset (Ref. 27).

process and the PL QY spectrum. We propose that this slow increase towards high E is partially caused by the inhomogeneity in E_T due to the conjugation length distribution known to exist in PPV films.[4] Also, singlet fission is more efficient at higher E due to resonant phonon emission, which may be described in a model similar to the Huang-Rhys process for the absorption spectrum.[25] Taking into account the two above-mentioned SF broadening processes we can fit the triplet QY action spectrum for $E > 3.1$ eV as shown in Fig. 4. The best fit is obtained with $E_T = 1.55$ eV and a Huang-Rhys parameter, $S_T = 1.5$.

The most efficient way, however, for obtaining E_T is by measuring the weak phosphorescence band, since the emission from $1\,^3B_u$ to the ground state ($1\,^1A_{gs}$) is only partially allowed due to the weak spin-orbit coupling in PPV. We note that phosphorescence in organics recently became important for display applications.[26] Since orgainc LED's today may use both singlet and triplet electroluminescence.

However, phosphorescence in PPV is elusive at best, since its probably extremely weak. Nevertheless ''heavy-atom'' effect may increase the emission from $1\,^3B_u$. If this will be achieved in future works then our findings gives the 0-0 transition of the phosphorescence band.

To complement the PPV energy levels we also measured the electroabsorption (EA) spectrum. For the EA measurements we used an ac electric field at frequency f to modify the electronic states of the material, and due to the quadratic effects in the centrosymmetric polymer, we measured the electric-field-induced changes ΔT at $2f$.[27] For applying the electric field onto the polymer film we used an interlocking finger electrode geometry with electrode separation of 40 μm.[27] There are three main EA spectral features seen in the PPV EA spectrum (Fig. 5).[28] At low $\hbar\omega$ there is a derivativelike feature that crosses zero at 2.58 eV, followed by two well pronounced phonon replicas at 2.77 and 2.96 eV, respectively. At higher $\hbar\omega$ there are two EA bands emerging at 3.4 and 3.7 eV, respectively, with no corresponding feature in the absorption spectrum. We conclude that these are due to strongly coupled even parity states mA_g and kA_g, with different relative strength, respectively. The transition $1A_g \rightarrow mA_g$ and $1A_g \rightarrow kA_g$ are symmetry forbidden, but the symmetry-breaking external electric field makes them par-
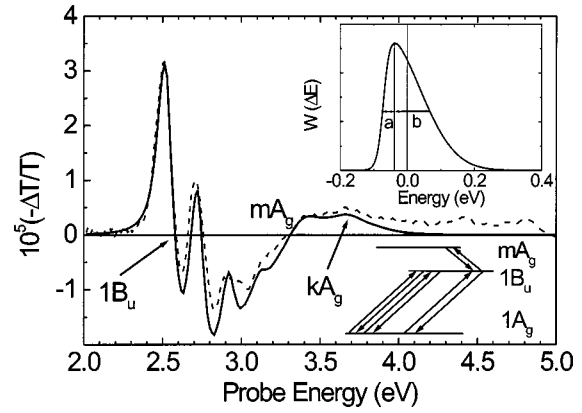
tially allowed by transferring oscillator strength from the $1A_g \rightarrow 1B_u$ transition.[29]

To a good approximation the measured EA spectrum is proportional to the imaginary part of the third-order susceptibility[27]

$$-\Delta T/T = \Delta\alpha d = \frac{4\pi\omega}{nc} \mathrm{Im}[\chi^{(3)}(-\omega,\omega,0,0]F^2 d, \quad (1)$$

where $\Delta\alpha$ is the change in the absorption coefficient α, ω is the photon frequency, n is the refractive index, c is the speed of light, and F is the applied electric-field strength. To calculate the optical susceptibility we used the summation over states (SOS) model recently developed for the EA in π-conjugated polymers.[27] By including four states in the calculation, namely $1A_g$, $1B_u$, and two even-parity states mA_g and kA_g, respectively, we could fit our EA spectrum as shown in Fig. 5. The best fit to our experimental data is obtained with the following parameters: $\bar{E}(1B_u) = 2.59$ eV, $\bar{E}(mA_g) = 3.40$ eV, $\bar{E}(kA_g) = 3.70$ eV, (where $\bar{E}$ denotes the average value of E in the film) and a phonon energy of 190 meV.

The existence of several strongly coupled A_g states in PPV type π-conjugated polymers was recently explained[30] by invoking other electronic bands, in addition to the traditional π-π^* bands. These are more localized electronic bands involving the phenylene group, that, nevertheless may add strongly coupled A_g states to the optical nonlinear spectra, including the EA spectrum.

What is obvious when inspecting the measured EA spectrum in Fig. 5 is the absence of Franz-Keldysh (FK) oscillations, as seen in polydiacetylene single crystals.[29] When the FK oscillations are destroyed by disorder, then $E(mA_g)$ may be considered the lower limit of the continuum band.[27] In this case, we may get an estimate of the exciton binding energy, E_b

$$E_b \geqslant E(mA_g) - E(1B_u) = 0.8 \text{ eV} \quad (2)$$

in good agreement with other EA measurements.[28]

Figure 3 summarizes the energy and optical transitions of the most important low-lying excited states in PPV studied

here. The energies in the singlet manifold were obtained from the PL onset ($PL_{0\text{-}0}$) and electroabsorption (EA) spectrum; in particular we obtained $E(1\,^1B_u) \simeq 2.45$ eV. We found $E(1\,^3B_u) = 1.55$ eV from the singlet fission threshold energy in the triplet QY excitation spectrum. We also found that the triplet state in PPV is quite localized, with a wave function extent of about 3.2 Å; this is consistent with its energy level deep inside the gap. The singlet/triplet energy splitting, Δ_{ST}, of the lowest excitonic state in PPV is therefore $\simeq 0.9$ eV. Since Δ_{ST} is determined by the exchange interaction, this large Δ_{ST} value shows that $e\text{-}e$ interaction in the prototype polymer PPV is relatively strong. Also since the T_1 transition is into the continuum band, or lower, i.e., into the $m\,^3A_g$ exciton (Fig. 3), we can get a lower limit estimate for the singlet exciton binding energy $E_b(\min)$ in PPV: $E_b(\min) = T_1 - \Delta_{ST} = 0.55$ eV. This value is in agreement with $E_b(=0.8$ eV) obtained from the EA spectroscopy.

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