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Site-selective fluorescence studies of poly(p-phenylene vinylene) and its derivatives

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We report fluorescence measurements on poly(p-phenylene vinylene), PPV, and four derivatives of this polymer, all of which show strong luminescence and can be used as emissive materials in electroluminescent diodes. We measure the variation of the emission spectrum with excitation energy at low temperature, and find a threshold energy above which emission is independent of excitation energy and below which the emission energy tracks with the excitation energy. This information makes it possible to separate out the effects of spectral diffusion by exciton migration from other forms of excited-state relaxation. We find that PPV and two derivatives with asymmetric, branches side chains show little or no excited-state relaxation. In contrast, the other two derivatives (one with bromine and dodecyloxy attachments at the two and five positions on the phenylene, the other with hexyloxy attachments at these sites, and cyano groups at the vinylic carbons) show further relaxation by about 0.25 eV. We consider that emission in these two polymers is from an interchain excimer excited state. Supporting evidence for the cyano-PPV is seen in the differences between the dilute solution and solid-state fluorescence spectra. [S0163-1829(96)00523-1]

INTRODUCTION

The optical properties of conjugated polymers have been of considerable interest in the past few years, since the discovery of electroluminescence from poly(p-phenylene-vinylene), PPV in a light-emitting diode (LED) structure.[1] An important feature of these materials is that their properties can be tuned by chemical modification. At present, PPV and several alkoxy- and cyano-substituted derivatives of PPV are being used to develop both higher efficiency LED's, and structures that have emission over different ranges of the visible spectrum. Luminescence in these materials is produced after either photoexcitation, or charge injection in an LED structure, when a neutral singlet excited-state decays in an allowed transition back to the ground state.

The nature of this excited state is however a contentious issue. If the excited state does not have a significant binding energy, then a band model description may be appropriate, but there are strong indications that the electron and hole are strongly bound, to form an intrachain exciton. In PPV, the best understood of these polymers, we consider that the balance of evidence shows that an exciton model is more appropriate. The coincidence of the onset of photoconductivity with the onset of optical absorption has been used to argue that the exciton is not strongly bound,[2–4] but this can also be explained by the creation of bound excitons, and their subsequent splitting to free carriers.[5,6] Also, the temperature dependence of the photoconductivity is consistent with an exciton binding energy of about 0.4 eV (Ref. 6). Site-selective fluorescence (SSF) studies on PPV (Refs. 7–10) provide evidence that the photoexcited states in the polymer are mobile neutral excitons, moving in a hopping process between polymer chains of different conjugation length. There is also direct evidence from time-resolved photoluminescence (PL) spectra in PPV and a soluble derivative, poly(2-methoxy, 5-(2'ethyl)-hexyloxy-p-phenylene-vinylene), MEH-PPV (see Table I), that there are polymer chains with a range of conjugation lengths (and hence excitation energies) in any sample.[11–14] The PL spectrum is much narrower than the absorption spectrum, and a redshift of the emission is observable over a few picoseconds after excitation, both of which indicate that excitations migrate to lower-energy regions before decaying.

In SSF experiments, the emission spectrum is measured as a function of the excitation wavelength. A threshold, known as the localization energy, occurs at a point fixed by the relative rates of exciton migration and decay. For photoexcitation above the localization threshold, the shape of the emission spectrum is independent of the excitation wavelength as excitons quickly migrate to sites of lower energy before decaying radiatively. As they move to chains of lower energy, the probability of being able to hop to other segments decreases until the hopping rate becomes comparable to the exciton decay rate. This defines the localization threshold below which excitons do not migrate, and hence we expect the emission energy to begin to decrease linearly with excitation energy, as emission occurs from the absorbing site.[7–10] Similar experiments have been performed on amorphous phosphorus,[15] an inorganic system that exhibits many of the features of organic polymer materials.

In conjugated polymer materials, the energy difference between absorption and luminescence is substantially due to exciton migration. Consequently, it is difficult to determine energy shifts due to any relaxation of the excited state prior to emission, a measurement which can give important information about the nature of the excitation. In SSF experiments, this difficulty is avoided as the excitation is localized to one site in the sample, and a measurement of the true energy shift between absorption and emission can be obtained. In short, SSF measurements provide important infor-

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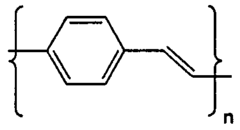
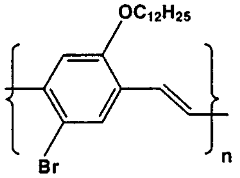
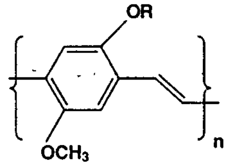
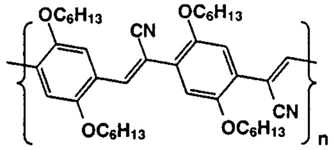
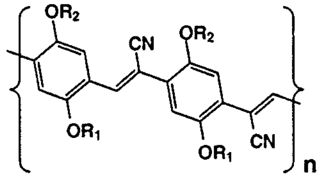
TABLE I. Structure, sample preparation details, and emission color of the polymers investigated.

Polymer	Structure	Spin cast from	Thermal conversion	Emission color	Refs.
PPV		methanol	10 h 250 °C	green	1
Br-PPV		chloroform	2 h 250 °C	red	25
MEH-PPV	 $R=CH_2CH(C_2H_5)(CH_2)_3CH_3$	chloroform	none	red	24
DHeO-CN-PPV		chloroform	none	red	26
MEH-CN-PPV	 $R_1=CH_3$ $R_2=CH_2CH(C_2H_5)(CH_2)_3CH_3$	toluene	none	orange / red	27

mation about the nature of the excited state responsible for luminescence in these polymer materials; for PPV, earlier measurements strongly suggest excitonic emission.[7–10]

In some other conjugated polymers, there is evidence for interchain excitations.[16–19] These have been interpreted in terms of excimer formation in the photoexcited state,[17–19] and in a cyano- derivative of PPV, DHeO-CN-PPV, (see Table I) Samuel, Rumbles, and Collision have recently suggested that luminescence comes from the decay of an interchain state, such as an excimer.[20] An excimer can be formed when an exciton on a polymer chain is stabilized by a charge-transfer interaction with another chain to form an excited-state complex. This complex will have different emission characteristics to an exciton, and a broad emission devoid of vibronic structure and redshifted compared to exciton emission is well-established in molecules such as pyrene.[21] In other conjugated polymers, particularly the ladder-type poly(phenylene)s there is clear evidence that the interchain interactions are present in the ground state, with absorption below the intrachain absorption edge giving rise to redshifted luminescence and photoconductivity, and are described as aggregate states.[22,23]

For many of the derivatives of PPV used in LED's, relatively little is known about the nature of the emissive excited state. In this investigation, we look at site selective fluorescence measurements on five of these materials. The polymers, which are summarized in Table I are MEH-PPV;[24] a bromine-substituted derivative of PPV, Br-PPV, which was synthesized with the intention of making a luminescent polymer with a large spin-orbit coupling factor to demonstrate (spin forbidden) triplet excited-state emission;[25] two high-electron affinity cyano-substituted derivatives of PPV, which have been used as electron transport and emissive layers in efficient two layer LED's,[26,27] which differ in the selection of the alkoxy groups attached to the phenylene rings, DHeO-CN-PPV having a symmetric dihexyloxy substitution, and

MEH-CN-PPV having the same asymmetric alkoxy groups as MEH-PPV; and PPV for comparison with the four derivatives. We discuss the results with reference to the nature of the excited state in the polymers.

EXPERIMENT

All measurements were performed on films of polymer spin cast from solution onto quartz substrates. PPV and Br-PPV are insoluble in their fully conjugated form and were hence spin cast as precursors and thermally converted to the polymer. Room-temperature optical absorption was measured with a Perkin Elmer Lambda 9 spectrophotometer. Low-temperature PL spectra were measured using a spectrograph coupled to a CCD array (ORIEL Instaspec IV) with the sample in a helium flow cryostat at 15 K. The excitation source was a monochromated 150-W xenon lamp with a full width at half maximum (FWHM) of the spectral output of 7 nm. PL spectra were recorded with excitation wavelengths ranging from 250 nm up to the tail of the optical absorption for each polymer. The spectral shape of the emission was found to be constant until excitation was in the tail of the absorption where the PL spectra began to move to longer wavelengths. The PL was weak here, so the CCD detector was set to perform integrated scans for each spectrum over a time typically in the range of 1–10 min. For comparison, some spectra were taken at room temperature using the same apparatus.

In previous investigations of this type, tuneable dye lasers have been used as the excitation source, with the advantage of a very narrow spectral output and high intensity.[7–10] Using a monochromated lamp, we have a lower spectral resolution, but the advantage of easier tunability.

RESULTS

Figure 1 shows the room-temperature absorption spectra [shown as -log(transmission), with no correction for reflection] for each polymer. The position of the peaks in absorption are 2.97 eV for PPV, 2.67 eV for Br-PPV, 2.51 eV for MEH-PPV, 2.53 eV for DHeO-CN-PPV, and 2.61 eV for MEH-CN-PPV. All are within a small range, except PPV, which has an absorption significantly blueshifted from the others. Vibronic structure is seen in the form of shoulders on the absorption band for PPV and Br-PPV, and arises from the coupling of the ring-stretching Raman-active mode that couples the ground-state and excited-state geometries. We note that the shape of the absorption spectrum for PPV is strongly dependent on the degree of order in the polymer, and PPV prepared via a modified route, in which a more rigid precursor polymer is processed, shows the peak absorption near 2.5 eV, which is associated with the pure electronic transition.[28] In contrast, the PPV used here shows a larger vibronic coupling, so that the peak absorption occurs for transitions involving two or three vibrational quanta.

Figures 2(a)–2(e) show PL spectra measured at room temperature and 15 K for each polymer, with the excitation energy near the peak of the optical absorption. In each we see that there is a redshift in the PL when the temperature is lowered. In the case of PPV, this has been assigned to the freezing out of ring rotation modes, which reduce the π band widths and hence increase the π-π^* gap.[28] MEH-PPV and PPV show vibronic structure at room temperature, with, respectively, two and three distinct peaks. This structure becomes better resolved at 15 K. The other polymers have broad featureless emission spectra at room temperature with some structure becoming apparent on cooling. DHeO-CN-PPV and MEH-CN-PPV have two features with the higher energy one appearing as a shoulder, and Br-PPV has a low- and high-energy shoulder around a central peak.

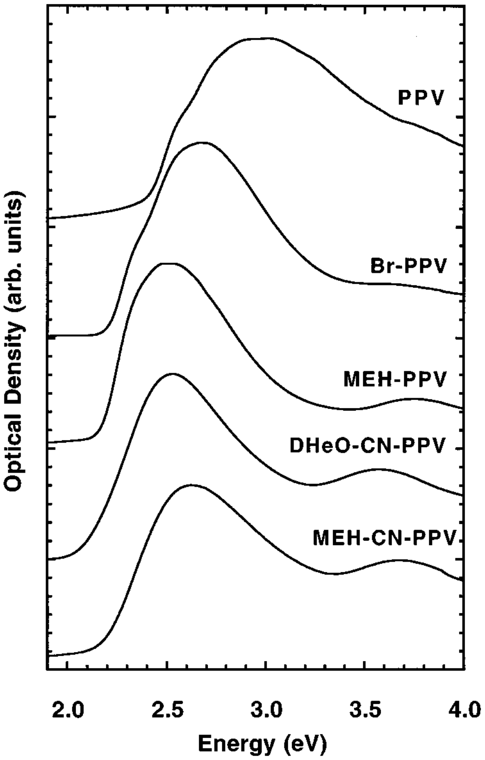


FIG. 1. The room-temperature solid-state optical-absorption spectrum for each polymer, normalized in height and offset for ease of comparison.

Careful efforts were made to find evidence for triplet emission at lower energies in the Br-PPV, which had been designed to incorporate a high atomic number element with a large spin-orbit coupling factor to facilitate the spin-forbidden triplet to ground-state electronic transition. There was, however, no evidence for such triplet state emission, which we would have expected to appear as a band of luminescence at a lower energy than the main feature. (Calculations for PPV suggest a value for such a transition from the lowest triplet to the singlet ground state at about 0.6- to 0.7-eV lower than the singlet emission[29].)

A series of PL spectra was measured at 15 K for each polymer with the excitation wavelength ranging from 250 nm up to the tail of the optical absorption. Figure 3 shows a number of these spectra normalized in height, and offset for clarity for; (a) PPV, and (b) DHeO-CN-PPV. These were recorded with long integrations on the spectrometer (spikes on the spectra are due to cosmic rays incident on the CCD array). Figure 3 illustrates the trend that in each polymer the PL shifts to lower energies as the excitation moves further into the absorption tail. For some spectra the excitation light began to overlap the PL, thus obscuring the highest-energy

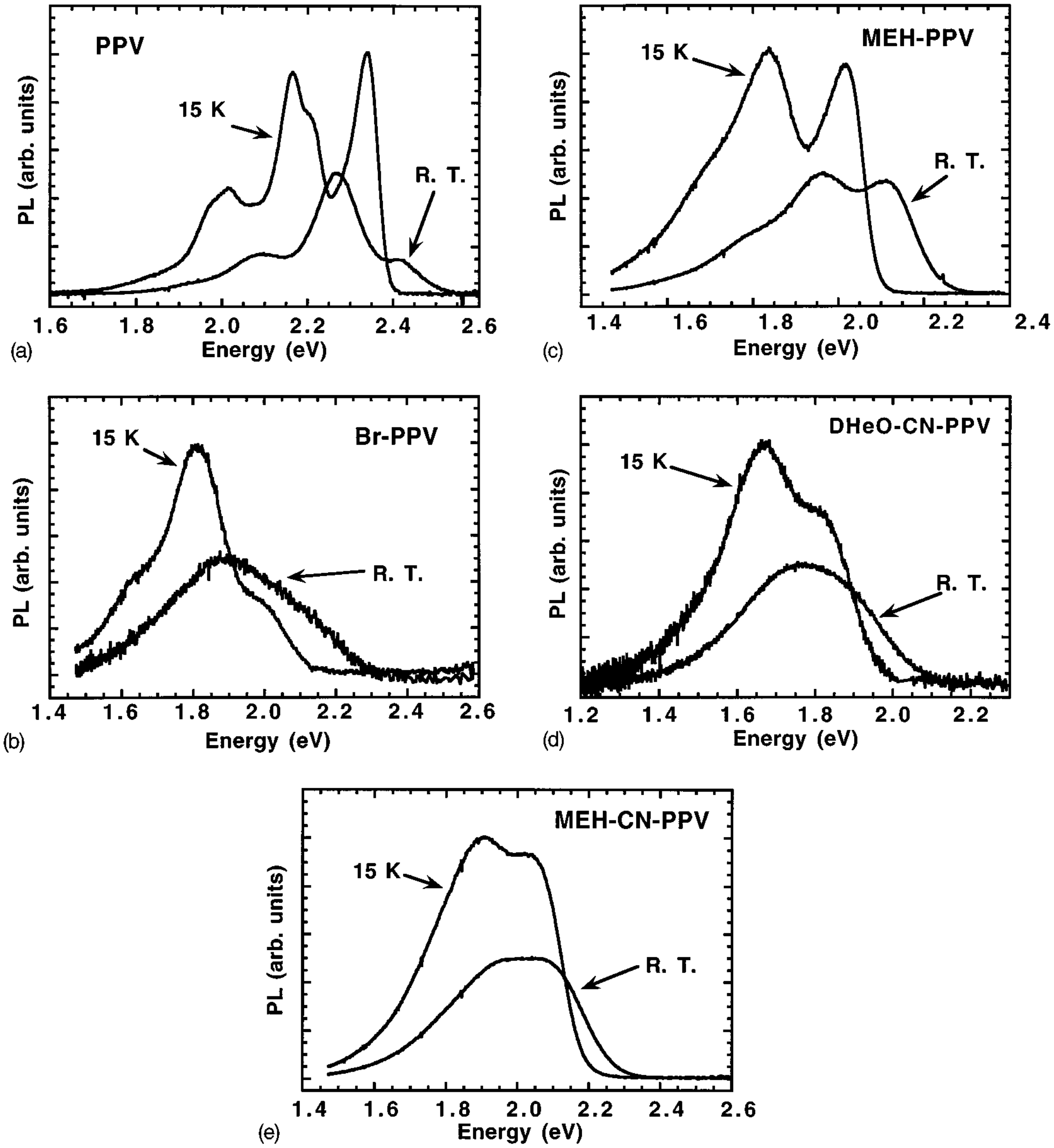


FIG. 2. Solid-state PL spectra measured at room temperature and 15 K for (a) PPV, (b) Br-PPV, (c) MEH-PPV, (d) DHeO-CN-PPV, (e) MEH-CN-PPV. The spectra are normalized, with the room-temperature curves half as high as those taken at 15 K.

vibronic feature. For this reason, in order to characterize the variation of emission energy with excitation energy, we chose to measure the position of the second highest-energy peak in each polymer, which we assign to the transition from the decay of a singlet electronic excited state with the loss of one phonon in the process. We use the notation $S_1 \rightarrow S_0$, $0 \rightarrow 1$ for this with $S_0 \rightarrow S_1$ representing the electronic transition, and $0 \rightarrow 1$ the associated transition between vibrational levels. A further trend visible in DHeO-CN-PPV and PPV is that structure in the spectra becomes more resolved with excitation at longer wavelengths. This is apparent in PPV as the small shoulder on the central vibronic peak becomes visible as a distinct peak itself.

Figure 4 summarizes the variation of emission energy with excitation energy in each polymer. It shows the spectral position of the second highest-energy peak in the PL spectra (the $0 \rightarrow 1$ phonon transition) plotted against excitation energy. In each material we see that, at high excitation energies, the peak position is independent of excitation wavelength, but below a threshold energy, the emission energy begins to decrease with decreasing excitation energy. (Measurements showing constant emission spectra were taken for excitation energies up to 4 eV in each polymer, but are not shown on the figure.) At room temperature, no dependence of the emission spectra on excitation wavelength was observed for any of the polymers.

The line indicating emission resonant with the excitation light is marked on the figure for reference. Also shown is the same line displaced by 0.18 eV, corresponding approximately to the vibrational energy generated in the $0 \rightarrow 1$ phonon transition [see Fig. 3(a) for PPV]. Straight lines have been drawn by eye through the points for each polymer to get an estimate of the gradient in each domain of response, since this gives a measure of the rate of decrease of emission with excitation energy. We define the localization threshold as the point at which the emission energy (E_{emis}) begins to decrease with excitation energy (E_{exc}), and the excitation energy at which this occurs the localization energy (E_{loc}).

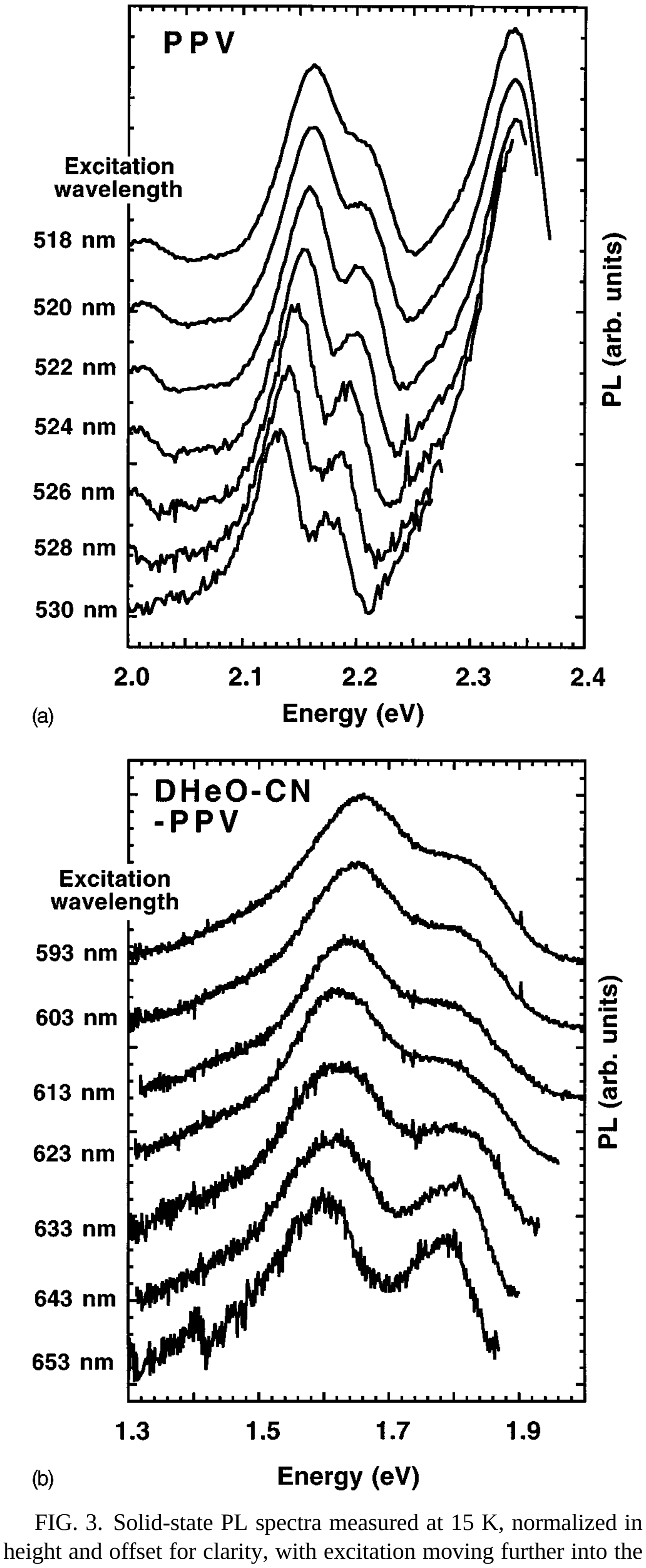


FIG. 3. Solid-state PL spectra measured at 15 K, normalized in height and offset for clarity, with excitation moving further into the tail of the absorption from top to bottom for, (a) PPV, (b) DHeO-CN-PPV. Some lower spectra are truncated where the excitation light began to overlap the PL. This is to avoid the large excitation peak obscuring other spectra.

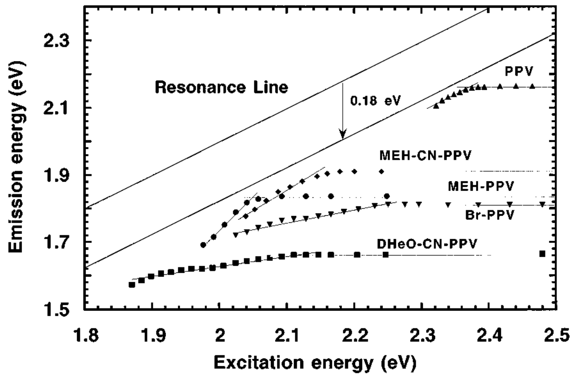


FIG. 4. Variation with excitation energy in the spectral position of the second highest-energy peak in the PL spectra (the $S_0 \rightarrow S_1/0 \rightarrow 1$ transition) of each polymer for excitation in the tail of the optical absorption. The solid line showing the position of emission resonant with the excitation light, and this line displaced by 0.18 eV (which represents the vibrational energy lost in the $0 \rightarrow 1$ phonon transition) are displayed for comparison.

The vertical difference between the localization threshold and the resonance line is a measure of the energy shift between excitation and emission, note that we have considered the second highest-energy vibronic peak in each polymer so no emission occurs close to resonance. Table II summarizes E_{loc}, the emission energy at E_{loc}, the energy shift, E_{loc}-E_{emis} between emission and resonance, and the gradient $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$ for each polymer.

PPV, MEH-PPV, and MEH-CN-PPV all have a redshift from excitation to emission for the $S_1 \rightarrow S_0/0 \rightarrow 1$ transition of between 0.21 and 0.25 eV. Most of this is due to the vibrational quantum generated in the emission process [$\approx$0.18 eV—see Fig. 3(a) for PPV], so that the Stokes' shift for these polymers is small. However, in the DHeO-CN-PPV and Br-PPV the shifts are much greater, 0.45 and 0.43, respectively.

The gradients $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$ vary widely between the different polymers. In PPV E_{emis} decreases linearly with E_{exc} below the localization threshold, and is in accord with earlier work.[7] MEH-CN-PPV has a gradient slightly greater than 1, but the other three materials show very different behavior. MEH-PPV has a gradient of 2.0, i.e., E_{emis} decreases twice as much as E_{exc} below localization. DHeO-CN-PPV and Br-PPV on the other hand both have shallow gradients, showing that E_{emis} is not so strongly dependent on E_{exc} in the localization regime.

DHeO-CN-PPV and MEH-CN-PPV differ only in the nature of the alkoxy substituents attached to the phenyl ring, and we see in Fig. 1 that they have similar absorption spectra. In the solid state, however, their emission spectra are very different, with DHeO-CN-PPV showing a redder luminescence, with an energy shift from absorption for the $S_1 \rightarrow S_0/0 \rightarrow 1$ transition of 0.45 eV compared to 0.23 eV in MEH-CN-PPV. Figure 5 compares the solid-state and dilute solution luminescence of the two materials. In contrast to the solid-state emission spectra, the solution spectra are almost identical. An explanation for this is that the emitting species for the two polymers are identical in solution, but are different in the solid state. This possibility is explored further in the following section.

DISCUSSION

The four derivatives of PPV studied in this work all have π-π^* energy gaps (indicated by the onset of the optical ab-

TABLE II. Summary of the localization energy (E_{loc}), the emission energy there (E_{emis}), the energy shift between absorption and emission (E_{loc}-E_{emis}), and the gradient in the localized regime $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$, obtained from the site-selective fluorescence measurements on each polymer.

Polymer	E_{loc} (eV)	E_{emis} (eV)	E_{loc}-E_{emis} (eV)	Gradient $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$
PPV	2.37	2.16	0.21	1.0
Br-PPV	2.24	1.81	0.43	0.39
MEH-PPV	2.05	1.84	0.25	2.0
DHeO-CN-PPV	2.11	1.66	0.45	0.29
MEH-CN-PPV	2.14	1.91	0.23	1.2

sorption), which are very similar to each other, but significantly lower than PPV itself. This is apparent in Fig. 1. Electron-donating substituents on the phenylene ring, such as alkoxy groups, which are present in all these derivatives, are known to lower the energy gap, giving a redshift in the absorption and emission as observed.[30] The addition of a cyano group onto the vinylic carbons, as in DHeO-CN-PPV and MEH-CN-PPV is not believed to effect the size of the optical gap.[30,31]

In these fluorescent polymers, the shape of the emission spectrum is determined by the nature of the emitting species, and the amount of inhomogeneous broadening. For emission from an excitonic state, we would usually expect some vibronic structure in the PL spectrum, whereas emission from an excimer state would produce featureless emission.[21] Inhomogeneous broadening is due to the emission from a range of conjugation lengths in the sample. This could, if severe, blue out vibronic structure in an emission spectrum.

Among the materials studied here, PPV and MEH-PPV have the most structured PL spectra, with well-defined vibronic features at low temperatures, suggesting excitonic emission. The structure is much sharper in PPV, which is known to have a high degree of crystallinity in the solid state.[32]

The other three polymers studied have relatively featureless emission spectra. This could be due to large inhomogeneous broadening effects, though the evidence for spectral diffusion above E_{loc} argues against this. Alternatively, this featureless emission could arise if it is due to the decay of a different excited species, such as an interchain excimer.[16–20] We consider that our site selective fluorescence measurements (Figs. 3 and 4, Table II) support the model of excimer emission for DHeO-CN-PPV and Br-PPV, although we are not yet able to explain all features of the data. The site-selective technique allows a measurement to be made of the true energy shift between absorption and emission for the excited state, a feature usually masked by exciton migration.

The energy shift between absorption and emission as measured here (second vibronic band is measured for emission) contains one vibrational quantum. It is known in PPV that the main phonons, which couple to the $S_1 \rightarrow S_0$ electronic transition, are phenyl ring-stretch modes at around 1600 cm^{-1} (≈ 0.2 eV), and the Stokes' shift in PPV has been found to be very small (≈ 12 meV),[7] or possible nonexistent.[9] This therefore explains an energy shift of about 0.2 eV between absorption and emission for PPV. In Fig. 2 we can see that the vibronic bands or shoulders that are visible in the PL spectra of the PPV derivatives are also separated by around 0.18-0.2 eV, hence we expect the loss of a phonon to contribute this amount to the energy shift in these polymers. In MEH-PPV and MEH-CN-PPV values of E_{loc}-E_{emis} are similar to PPV (Table II), suggesting similar modes of excited-state relaxation and emission, i.e., excitonic emission with small Stokes' shift.

DHeO-CN-PPV and Br-PPV however have a much larger shift E_{loc}-E_{emis} (Table II), around twice that seen in the other polymers. There are several possible explanations for this, including the following.

(i) The $S_1 \rightarrow S_0/0 \rightarrow 0$ transition may be very weak, so that it is undetected in our spectra, so that we have measured the $S_1 \rightarrow S_0/0 \rightarrow 2$ peak, but assigned it to the $S_1 \rightarrow S_0/0 \rightarrow 1$ peak, thereby accounting for the extra 0.2 eV. There is no reason to suppose that the Frank-Condon factors should be very different for these polymers, and we do not consider that this is a likely explanation here.

(ii) The energy could be lost by relaxation of the excited-state geometry and the emission of low-energy phonons prior to emission. Such a process might be a substantial ring rotation. The smaller energy shifts seen for DHeO-CN-PPV in solution (Fig. 5) are not, however, consistent with this model.

(iii) The formation of an interchain excited state with a lowered energy, such as an excimer could also produce such

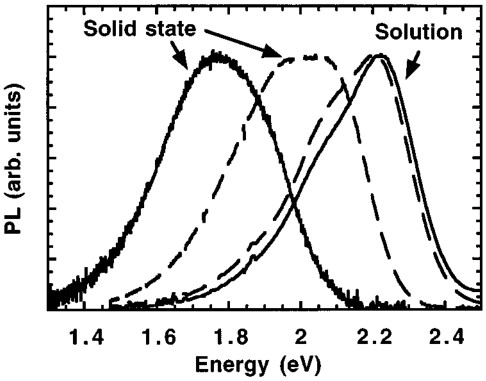


FIG. 5. A comparison of dilute solution and solid-state PL spectra measured at room temperature for DHeO-CN-PPV (full line) and MEH-CN-PPV (broken line). The solutions were, DHeO-CN-PPV 25 mg l^{-1} in chloroform; MEH-CN-PPV 16 mg l^{-1} in chloroform. Further dilution did not change the shape of the PL spectrum in either case. The excitation source for the solution spectra was the 457-nm line of an Ar^{+} laser.

an energy loss. The excimer state is a charge-transfer complex between two (or possible more) polymer chains, which is lower in energy than the exciton state where the excitation is confined to one chain.

We consider that the excimer model (iii) is the best explanation for the emission characteristics of Br-PPV and DHeO-CN-PPV. It explains not only the large energy shift between absorption and emission, but also the broad featureless emission spectra. For DHeO-CN-PPV, time-resolved luminescence measurements[20] support this picture. Further support is provided by the solution and solid-state PL spectra shown for this polymer and MEH-CN-PPV in Fig. 5. Here we see that chemically similar polymers, with very similar solid-state absorption and dilute solution PL spectra, have different solid-state PL spectra. A redshift in the PL as seen here in MEH-CN-PPV on going from solution to solid state is commonly observed for polymers of this type, and is attributed to increased conjugation length from improved ordering in the solid state.[33] Intrachain exciton emission is responsible for the luminescence from both polymers in dilute solution where the existence of interchain species is unlikely due to large chain separation. We consider that the solid-state PL is redshifted from the solution spectrum as a result of ordering in MEH-CN-PPV, but is still due to intrachain excitons, but is further redshifted in DHeO-CN-PPV as a result of excimer formation. The large redshift in DHeO-CN-PPV cannot be explained in terms of a large increase in conjugation length in the solid state, because this would similarly affect the absorption. The fact that the energy shift E_{loc}-E_{emis} from absorption to emission in the two polymers is very different shows that this is not the case. [Note that this solution/solid-state comparison cannot be done on Br-PPV, because films are prepared from a nonconjugated precursor polymer.]

We comment also on the gradients $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$ measured in the localized regime for each polymer (Table II). For excitation below E_{loc} the excited state is localized, and emission comes from the absorbing site, so we would expect it to shift linearly with E_{exc}. This is what we observe in PPV, in agreement with earlier measurements. The gradient in MEH-CN-PPV is also close to 1, and can be explained in the same way. The results in the other derivatives of PPV are more puzzling. DHeO-CN-PPV and Br-PPV both have gradients less than 1, i.e., E_{emis} is not as strongly dependent on E_{exc} as we would expect. This could be explained in the model of excitonic emission with a large Stokes' shift if the shift decreases as sites of lower energy are excited. We note that measurements on PPV oligomers show that there is a trend towards smaller Stokes' shifts in longer molecules.[34]

Our preferred model is however that we are observing emission from an interchain state, such as an excimer. Interchain excitations are less mobile than singlet excitons,[20] and we consider for these states that since the large redshift in emission is due to interchain electron delocalization, they will be less sensitive to the extent of intrachain delocalization (conjugation length). In these site-selective measurements if the absorption is to an exciton state strongly dependent on conjugation length, but the emission from an excimer less dependent, this would give a shallow gradient $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$, such as we observe.

We are not at present able to explain the gradient of $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}=2$ for MEH-PPV. The Stokes' shift would seem to be increasing as we excite sites of lower energy in this polymer. It is possible that when we are exciting far down in the tail of the absorption, we absorb at sites that are very distorted and show a large relaxation around the excited state.

CONCLUSIONS

We have compared the emission characteristics of four PPV derivatives with PPV, using site-selective fluorescence measurements, as well as contrasting dilute solution and solid-state PL spectra for the two most chemically similar polymers. We believe that we have convincing evidence for emission from an interchain charge-transfer state such as an excimer in Br-PPV and DHeO-CN-PPV. Both polymers have broad featureless emission spectra with a large energy loss between absorption and emission, and shallow $\Delta E_{\mathrm{emis}}/\Delta E_{\mathrm{exc}}$ gradients in the localized regime. The conclusion is supported for DHeO-CN-PPV by the observation that it has a PL spectrum very similar to MEH-CN-PPV in solution, but is considerably redshifted in the solid state. This comparison suggests that the different alkoxy side chains on these two polymers effects packing of the chains in the solid state to such an extent to allow excimer formation in DHeO-CN-PPV, but not in MEH-CN-PPV.

Our results show that interchain interactions can have a strong effect on luminescence in conjugated polymers and must be considered for the design of highly fluorescent materials. Furthermore, the results suggest that tuning of the solid-state emission characteristics of these polymers can be achieved by altering side-group substituents, which affect the way the chains pack together, as well as the more traditional method of chemical modification of the band gap.

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[1] J. H. Burroughes *et al.*, Nature **347**, 539 (1990).

[2] J. Obrzut, M. J. Obrzut, and F. E. Karasz, Synth. Met. **29**, E103 (1989).

[3] T. Takiguchi *et al.*, Synth. Met. **17**, 657 (1987).

[4] C. H. Lee, G. Yu, and A. J. Heeger, Phys. Rev. B **47**, 15 543 (1992).

[5] E. L. Frankevich *et al.*, Phys. Rev. B **46**, 9320 (1992).

[6] R. N. Marks *et al.*, J. Phys. Condens. Matter **6**, 1379 (1994).

[7] U. Rauscher *et al.*, Phys. Rev. B **42**, 9830 (1990).

[8] H. Bässler *et al.*, Synth. Met. **49**-**50**, 341 (1992).

[9] S. Heun *et al.*, J. Phys. Condens. Matter **5**, 247 (1993).

[10] U. Rauscher *et al.*, J. Phys. Condens. Matter **1**, 9751 (1989).

[11] I. D. W. Samuel *et al.*, Synth. Met. **54**, 281 (1993).

[12] I. D. W. Samuel *et al.*, Chem. Phys. Lett. **213**, 472 (1993).

[13] R. Kersting *et al.*, Phys. Rev. Lett. **70**, 3820 (1993).

[14] G. R. Hayes, I. D. W. Samuel, and R. T. Phillips, Phys. Rev. B **52**, 11 569 (1995).

[15] D. Wolverson, Z. Sobiesierski, and R. T. Phillips, J. Phys. Condens. Matter **2**, 6433 (1990).

[16] M. Yan *et al.*, Phys. Rev. Lett. **73**, 744 (1994).

[17] S. A. Jenekhe and J. A. Osaheni, Science **265**, 765 (1994).

[18] J. Bisberg *et al.*, Macromolecules **28**, 386 (1995).

[19] A. Tsuchida, T. Ikawa, and M. Yamamoto, Polymer **36**, 3103 (1995).

[20] I. D. W. Samuel, G. Rumbles, and C. J. Collision, Phys. Rev. B **52**, 11 573 (1995).

[21] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Clarendon, Oxford, 1982).

[22] U. Lemmer *et al.*, Chem. Phys. Lett. **240**, 373 (1995).

[23] A. Köhler *et al.*, Chem. Phys. Lett. **243**, 456 (1995).

[24] D. Braun and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).

[25] G. J. Sarnecki *et al.*, Synth. Met. **69**, 545 (1995).

[26] N. C. Greenham *et al.*, Nature **365**, 628 (1993).

[27] D. R. Baigent *et al.*, Synth. Met. **67**, 3 (1994).

[28] K. Pichler *et al.*, Synth. Met. **55-57**, 230 (1993).

[29] D. Belionne *et al.*, J. Chem. Phys. **102**, 2042 (1995).

[30] J. L. Brédas and A. J. Heeger, Chem. Phys. Lett. **217**, 507 (1994).

[31] M. Fahlman *et al.*, J. Chem. Phys. **102**, 8167 (1995).

[32] J. H. F. Martens *et al.*, Synth. Met. **55-57**, 434 (1993).

[33] C. L. Gettinger *et al.*, J. Chem. Phys. **101**, 1673 (1994).

[34] H. S. Woo *et al.*, Synth. Met. **59**, 13 (1993).