Invited Paper

Photoluminescence in poly(3-hexylthiophene)

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ABSTRACT

We report a study of the photophysics of solutions and films of the conjugated polymer poly(3-hexylthiophene) (P3HT). We have performed measurements of absorption, photoluminescence (PL), PL quantum yield, and time-resolved PL. For P3HT in a good solvent the PL decays with a time constant of 510±20 ps, and the PL quantum yield is 0.42±0.04. we assign the PL to the intra-chain singlet exciton, and deduce a natural radiative lifetime for this species of 1.2±0.1 ns. We explore the use of solvent mixture as a way of controlling the degree of intermolecular interaction. We find that there is a red-shift of absorption and PL in poor solvent mixtures, and the spectra and PL quantum yield become similar to the film. The PL decay becomes faster and non-exponential in poor solvent mixtures and the thin film.

Keywords: photoluminescence, quantum yield, poly(3-hexylthiophene), solvatochromism, time-resolved spectroscopy, singlet exciton

INTRODUCTION

Conjugated polymers are an important class of organic semiconductor in which the π-electrons are delocalised along the polymer chain[1,2]. This gives the materials one-dimensional character and the possibility of forming self-localised excitations such as polarons. There have been many studies of the photophysics of conjugated polymers, but several aspects remain controversial. An improved understanding of the photophysics is not only of fundamental interest but also of practical importance following the discovery that conjugated polymers can be used as the active layer in light-emitting diodes[3]. This is now a very promising display technology which could give flat large area colour screens with excellent visibility.

There is currently a debate as to whether the dominant photoexcitation in conjugated polymers is intra-molecular (resides on a single polymer chain) or inter-molecular (is delocalised over two or more polymer chains) in character[4-20]. The most widely studied luminescent polymer is poly(*p*-phenylenevinylene), PPV. The photoluminescence (PL) of this material has been assigned to the radiative decay of the (intra-chain) singlet exciton, and it has been proposed that this is the dominant product of photoexcitation[4]. Rothberg, Conwell and co-workers accept the assignment of the PL to the singlet exciton, but argue on the basis of measurements of transient absorption, transient PL and stimulated emission, that polaron pairs are the dominant product of photoexcitation[9-12]. Polaron pairs in PPV are a non-emissive inter-molecular excitation, and it is proposed that approximately 90% of photons absorbed lead to their generation (i.e. that only 10% of absorbed photons generate the singlet exciton). Greenham *et al* [6] examined this carefully using a combination of measurements of PL efficiency and time-dependence on the same samples. They found very strong evidence that the singlet exciton is the dominant photoexcitation and is generated with a quantum yield in the range 90-100%. The incompatibility of these results could be due to differences in the materials studied. For example the synthesis, film preparation, and conversion conditions could all have an effect. In addition it has been shown that photo-oxidation has a strong effect on PL[21,22]. Alternatively the differences could be due to the very high excitation densities used in transient absorption and stimulated emission measurements[23,24].

The work of Greenham *et al* shows convincingly that intra-chain excitons are the dominant product of photoexcitation in PPV films prepared in Cambridge. More recently we have studied a cyano-substituted PPV derivative, referred to as CN-PPV[13]. This molecule has a cyano group attached to the vinylene linkage and two hexyloxy substituents on the phenylene ring. The aim of the cyano group was to increase the electron affinity of the material, and so to facilitate the injection of electrons in polymer LEDs. The hexyloxy substituents confer solubility in common organic solvents such as toluene and chloroform. These modifications to the PPV molecule were very successful, and gave substantial improvements in the efficiency of LEDs incorporating CN-PPV. The PL quantum yield of CN-PPV in toluene solution is 52±5%, and the decay of the PL is dominated by a component of 0.9±0.1 ns time-constant. These data imply a natural radiative lifetime of 1.7±0.2 ns and are fully compatible with emission being from intra-chain singlet excitons. The situation in films of CN-PPV is very different[13]. The PL is much longer-lived than in

solution, with a decay dominated by a component of time-constant 5.6±0.2 ns. When combined with the PL quantum yield of the film of 0.35±0.03, this implies a natural radiative lifetime of 16±2 ns. This is an order of magnitude more than for other examples of conjugated polymers discussed above, and shows that the emitting species is weakly radiatively coupled to the ground state. In addition the luminescence spectrum of the film is broad, structureless and red-shifted. The results can be explained as emission from the solution being from the intra-chain singlet exciton, but emission from the film being from an inter-molecular excitation such as an excimer or physical dimer.

The formation of excimers is well known in aromatic molecules[23-26]. There is also evidence for emission from excimers or aggregates in a number of other conjugated polymers and oligomers including ladder-type poly(*p*-phenylene)[18,19], polybenzobisthiazoles[17], and sexithiophene[27]. The point we wish to emphasise is that in some conjugated polymers the luminescence is from an inter-molecular excited state. The question of whether it is an aggregate or an excimer is of secondary importance.

The ideal experimental technique for investigation of these issues of intra- and inter-chain excitations would be a way of controlling inter-molecular interactions. We would like to be able to look at the limits of no inter-molecular interaction, and strong inter-molecular interaction, and to tune continuously between them. To achieve this is a very challenging problem as it requires control over the organisation of molecules on atomic length-scales. One possible approach is to study a conjugated polymer in solution, and to change the solvent. A good solvent will favour isolated polymer chains (i.e. no intermolecular contact), whereas a poor solvent will favour aggregation (strong inter-molecular contact). Hence changing the solvent can be used to change the degree of inter-molecular interaction. Finer control could be achieved by using mixtures of good and poor solvents and changing the relative proportion of the solvents. Yoshino and co-workers have shown that solvent mixture can change the intermolecular spacing in gels of poly(3-hexylthiophene)[28,29].

There have been a number of studies of the photophysics and electroluminescence of poly(3-alkylthiophene)s[15,16,28-36]. In this paper we examine the photophysics of poly(3-hexylthiophene) (P3HT, see figure 1) using a combination of measurements of luminescence efficiency and time-dependence, as well as steady-state absorption and luminescence. We explore the effect of good and poor solvent mixtures on the photophysics of P3HT.

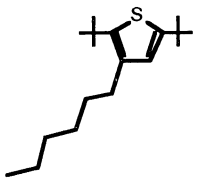

Figure 1: The poly(3-hexylthiophene) molecule

EXPERIMENTAL

The polymers were prepared by a McCullough type chemical synthesis giving control over the regioregularity[37,38]. 95% head to tail coupling could be achieved by this approach. Absorption and PL spectra were measured using commercial spectrometers. Solutions were prepared using HPLC grade solvents. The peak absorbance of solutions used for optical measurements was not more than 0.1 cm^{-1}. The PL quantum yield of solutions was measured by the method of Williams *et al*[39], using Rhodamine 101 (which has a PL quantum yield of 1) as a standard. Toluene was used as a good solvent for the P3ATs, and methanol was used as a poor solvent. Thin films were prepared by spin-coating from chloroform solution. Their PL quantum yield was measured using an integrating sphere, following the procedure described by Greenham *et al.*[6].

Time-resolved luminescence measurements were made by the time-correlated single photon counting technique[40]. The sample was excited by a modelocked and cavity dumped dye laser giving light pulses of 10 ps duration at a repetition rate of 4 MHz. The PL was collected in 90° geometry and passed through a polariser and subtractive dispersion monochromator to a microchannel plate photomultiplier detector. The full width at half maximum of the instrument response function was 70 ps. Data analysis was performed by a nonlinear least-squares iterative reconvolution procedure. Goodness of fit was judged by the reduced chi-square (<1.3), the serial correlation coefficient (>1.7), and a random plot of weighted residuals. An important feature of this experiment is its single-photon sensitivity, which means that measurements are made at much lower excitation intensities than other techniques. The average power is typically of order 0.1 W/cm^2, corresponding to a peak power of 3 kW/cm^2 - orders of magnitude less than used in most other time-resolved measurements. This minimises problems with photodegradation and bimolecular processes such as exciton-exciton annihilation.

RESULTS

The absorption spectrum of P3HT in a range of solvent mixtures is shown in figure 2. Mixtures of toluene and methanol were used, with the volume fraction of toluene in the range 100% to 17%. The polymer concentration was the same for all the curves shown. The absorption spectrum of P3HT in neat toluene is smooth and peaks at 450 nm. The spectrum for 75% toluene is very similar. As the volume fraction of toluene decreases below 75% (i.e. the methanol fraction increases above 25%), the absorption spectrum shifts to the red and gains vibronic structure. For 17% toluene, the peak has shifted to 510 nm. Increasing the fraction of methanol leads to a decrease in absorbance at shorter wavelength, and an increase at longer wavelength, with an isosbestic point at 475 nm. The absorption spectrum in the poor solvent mixture (17% toluene) is similar to that of a thin solid film, as shown in figure 3.

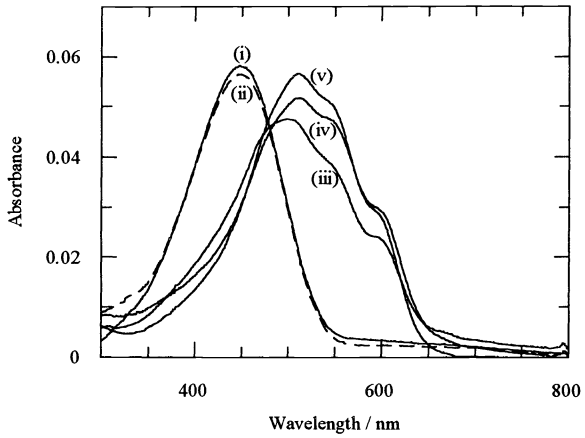

Figure 2: Absorption spectra of P3HT in toluene/methanol mixtures of (i) 100%/0% (ii) 75%/25% (iii) 50%/50% (iv) 25%75%, and (v) 17%/83%.

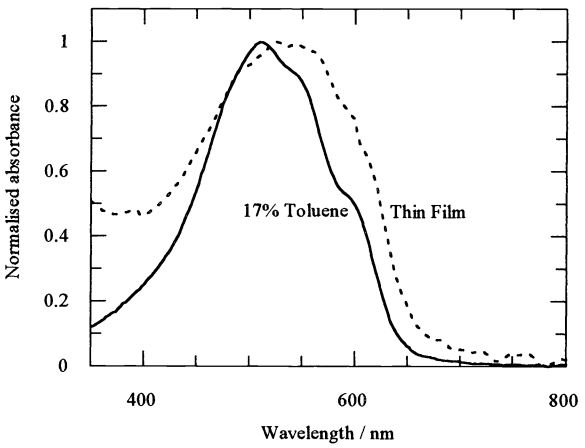

Figure 3: Comparison of absorption spectra of P3HT in 17% toluene solution and thin film

The photoluminescence spectra of P3HT as a function of solvent mixture are shown in figure 4(a). The spectra shown are once again at the same concentration. The spectra in neat toluene and 75% toluene are identical, as in the case of absorption. However, as the toluene fraction decreases, there is a dramatic drop in PL intensity, accompanied by a red-shift of the emission. The PL quantum yield falls from 0.42±0.04 in neat toluene to 0.01±0.006 in the 17% toluene mixture. For comparison the PL quantum yield of a P3HT thin film is 0.02±0.004.

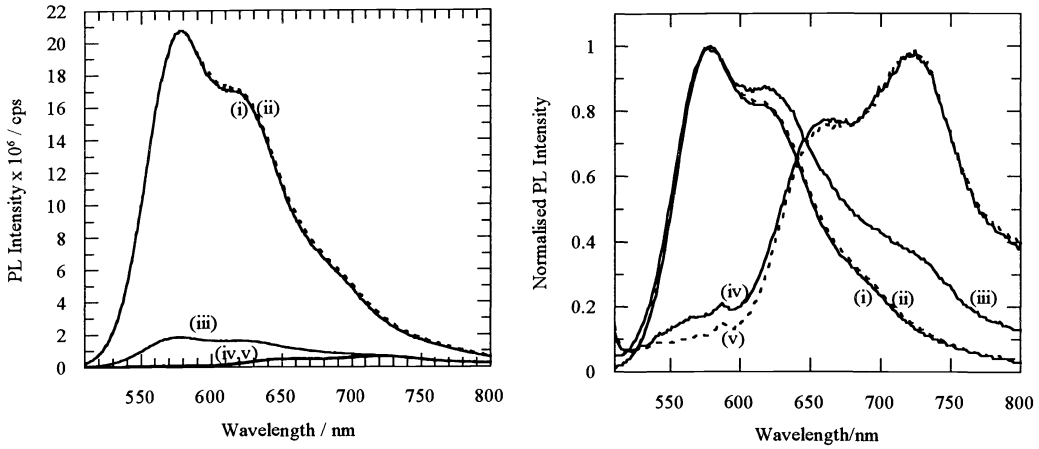

Figure 4(a) (left panel): Photoluminescence spectra of P3HT in toluene/methanol mixtures of (i) 100%/0% (ii) 75%/25% (iii) 50%/50% (iv) 25%/75%, and (v) 17%/83%.
Figure 4(b) (right panel): The spectra of figure 4(a) normalised to the same peak intensity

The shape of the spectra can be seen more clearly in figure 4(b) which shows the spectra normalised to equal peak intensity. The peak of the PL is at 580 nm in a good solvent environment (100% or 75% toluene), and at 720 nm in a poor solvent mixture (25% or 17% toluene). There is clear vibronic structure in all the spectra and a change in the relative weight of the vibronic features contributes to the red-shift. Like the absorption spectra, these curves can be represented as a linear combination of a shorter-wavelength and longer-wavelength species. The PL spectrum in 17% toluene is similar to that of the thin film, as can be seen from figure 5.

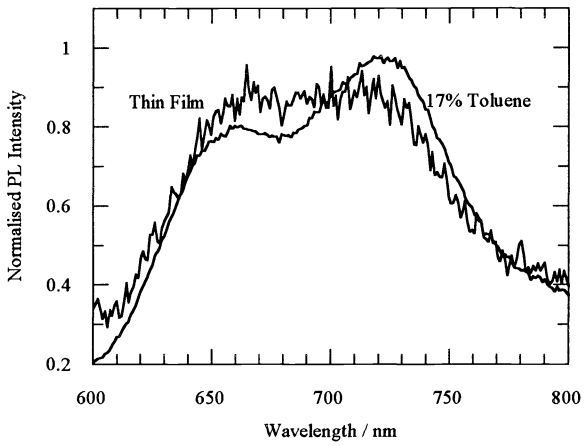

Figure 5: Comparison of photoluminescence spectra of P3HT in 17% toluene solution and thin film

The results of time-resolved luminescence measurements are shown in figure 6. In neat toluene, the decay is described well by a single exponential of time constant 510±20 ps. In 17% toluene, and in the thin film, the decay of the PL is faster. The decay kinetics are complicated and can only be satisfactorily fitted by a sum of three exponentials. The resulting curve-fits are summarised in table 1.

For the thin film with excitation (624 nm) and detection (700 nm) polarisations parallel, the time-constants (and pre-exponential factors) obtained are 80 ps (0.51), 220 ps (0.40), and 520 ps (0.09). The main features of the decays are similar for perpendicular polarisations of excitation and detection, and for other emission wavelengths. The components with the largest pre-exponential factors are much shorter-lived than for the P3HT in (100%) toluene solution, and there is a small longer-lived component with time constant similar to that of the toluene solution.

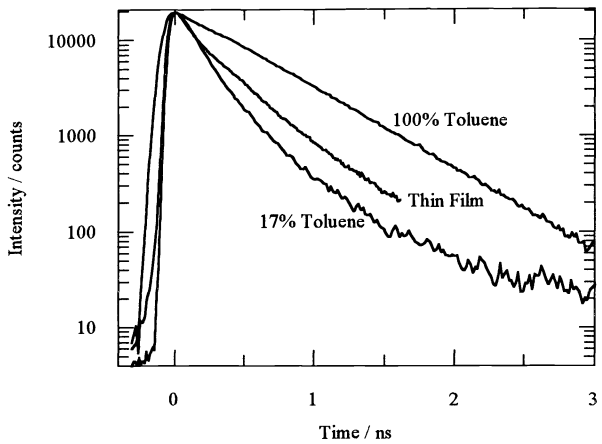

Figure 6: Time-resolved PL of P3HT

For P3HT in a poor solvent mixture of 17% toluene excited at 635 nm, the table shows data for emission wavelengths of 700 nm, 750 nm, and 800 nm. We have performed a "global" analysis of these data in which one set of time constants is fitted to the three sets of data. For the case of emission at 700 nm, we obtain time constants (and pre-exponential factors) of 25 ps (0.81), 190 ps (0.18), and 590 ps (0.01). Hence the two main components of the decay are faster than for P3HT in (100%) toluene solution.

P3HT	Φ	a_1	τ_1/ns	a_2	τ_2/ns	a_3	τ_3/ns	χ^2
100% toluene solution	0.42	1	0.51	-	-	-	-	1.0
Thin film	0.02	0.51	0.08	0.40	0.22	0.09	0.52	1.0
17% toluene 700 nm	0.01	0.81	0.025	0.18	0.19	0.01	0.59	1.4
17% toluene 750 nm	"	0.74	"	0.24	"	0.02	"	1.2
17% toluene 800 nm	"	0.77	"	0.21	"	0.03	"	1.2

Table 1: Summary of PL quantum yield (Φ) measurements and three-exponential curve-fits to time-resolved PL in P3HT. a_1, a_2, and a_3 are the pre-exponential factors; τ_1, τ_2, and τ_3 are the corresponding time-constants.

DISCUSSION

The changes in absorption spectrum with solvent mixture, suggest that the conformation of the polymer depends on the solvent used. The longer-wavelength absorption in poor solvent mixtures (i.e. small volume fraction of toluene) indicates that the chains are more conjugated. This could arise from the polymer chains being much straighter in poor solvents. The presence of the isosbestic point means that the absorption spectrum can be considered as a linear combination of two species: polymer in a good solvent, and polymer in a poor solvent. The similarity of the absorption of the thin film and the poor solvent mixture suggests that the arrangement and conformation of the polymer molecules is similar in these two environments. These results are similar to our previous work on chromism in poly(3-dodecylthiophene) (P3DT)[16].

The PL spectra, like the absorption, also undergo a substantial red-shift in a poor solvent mixture. The longer wavelength emission again suggests that the polymer chains are more conjugated in the poor solvent mixture. The PL spectra can be expressed as a linear combination of two species, although there is a substantial difference in their quantum yields. The PL spectra and quantum yields of the poor solvent mixture and the film are similar, again suggesting that the arrangement and conformation of the molecules is similar in these two environments.

We note that solvatochromism has been extensively studied in soluble polydiacetylenes[41-43], although there is some disagreement about its interpretation. The PL quantum yield is higher in the P3ATs so that we can learn about solvatochromism from luminescence as well as absorption. Possible causes of the red-shifted spectra are that the polymer chains form isolated rigid rods, single-chain fringe micelles, or aggregates. Our data go some way towards distinguishing between these possibilities. The similarity of the red-shifted solution spectra (analogous to the R-form in polydiacetylenes) to the film spectra suggests a similar environment in both cases. This is consistent with an aggregate or fringe micelle (intra-molecular aggregate). Whether the species are single chains or multiple chains is difficult to argue as both would appear spectroscopically similar. The solutions used here are very dilute and aggregation would take some time to occur. Our spectroscopic observations are immediate upon

production of the solvent mixture, but over a 24 hour period the absorbance of the 17% toluene solution falls substantially. We interpret this as large multiple chain aggregate formation followed by precipitation.

Excited states in conjugated polymers can decay by a combination of radiative and non-radiative processes, and the relative rate of these processes determines the efficiency of luminescence. We can model these processes by rate constants k_R and k_{NR} describing radiative and non-radiative decay, and the PL quantum yield, Φ, will then be given by:

$$\Phi = \frac{k_R}{k_R + k_{NR}} = \frac{\tau}{\tau_R} \quad (1)$$

The lifetime of the PL, τ, is given by

$$\tau = \frac{1}{k_R + k_{NR}} \quad (2)$$

and $\tau_R = 1/k_R$ is the natural radiative lifetime i.e. the lifetime the PL would have in the absence of non-radiative decay.

For P3HT in a good solvent (100% toluene), the measured PL quantum yield (0.42) and PL decay time (510 ps) imply a natural radiative lifetime of 1.2±0.1 ns. This is typical of a fully allowed transition in a strongly absorbing material, and we assign the PL to emission from the (intra-chain) singlet exciton. Emission from singlet excitons has been seen in a number of systems such as PPV thin films[4,6], poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) in solution[8], CN-PPV in solution[13,44] and the model oligomer *trans,trans*-distyrylbenzene[45]. All these systems have natural radiative lifetimes in the range 0.9-1.7 ns. The natural radiative lifetime of highly regioregular and less regioregular forms of P3DT[16] are also in this range. It appears that the PL from well-solvated conjugated polymer chains is always due to (intra-chain) singlet excitons.

We next consider the observation that the PL quantum yield is a factor of 20 lower in the film than in 100% toluene solution, and a factor 40 lower in poor solvent mixtures than in the 100% toluene solution. The large drop in PL quantum yield could arise from a large increase in the rate of non-radiative decay processes, or a substantial fall in the rate of radiative decay. An increase in the rate of non-radiative decay could occur if there are additional non-radiative decay pathways in the thin film. A decrease in the rate of radiative decay could arise if the emitting species in the thin film is an inter-molecular excitation with reduced oscillator strength. There is some precedent for this in CN-PPV, where the radiative rate constant is an order of magnitude lower in the thin film than the solution[13,46].

In previous work we have been able to use a combination of measurements of PL quantum yield and time-dependence with equations 1 and 2 to deduce k_R and k_{NR}. Unfortunately, in thin films and poor solvent mixtures of P3HT, the non-monoexponential PL kinetics means that the decay of the emitting species cannot simply be described by rate constants and we therefore cannot apply this analysis. There are a number of processes which can cause non-monoexponential decay kinetics. One possibility is that there is a distribution of environments of the emitting species, and a related possibility is that there is "spectral diffusion" in which excitations migrate between different environments. Another possible explanation is that there is more than one emitting species. Alternatively there could be a non-exponential decay process such as diffusion of excitations to quenching sites.

We can consider the thin film data further, and assume to begin with that there is a single emitting species with the same natural radiative lifetime (1.2 ns) as for the 100% toluene solution. If the fall in PL quantum yield is entirely due to an increase in non-radiative decay, then a decay time of 24±5 ps would be expected. This is significantly faster than the fastest component (80 ps) of the measured PL decay. We have previously proposed[15,16] on the basis of the average PL lifetime that the fall in PL quantum yield is a result of a decrease in radiative rate constant due to an inter-molecular excitation. However, it would not account for the 80 ps component of the decay, unless accompanied by an increase in non-radiative decay rate, and even then a distribution of environments in the sample would be needed to account for the non-exponential decay. Unfortunately, the non-monoexponential decay means that we cannot deduce rate constants, and hence cannot distinguish between these possibilities.

Similar arguments apply to P3HT in a poor solvent mixture. For a single emitting species with the same natural radiative lifetime (1.2 ns) as for the 100% toluene solution, the observed PL quantum yield would imply a PL decay of time constant 12±7 ps decay. There is a substantial component of the PL decay consistent with this (considering that we are at the limit of the time-resolution of the apparatus). It may be possible to associate this with very poorly solvated material and then to explain the longer-lived parts of the decay as being due to better-solvated parts of the sample. However, as in the case of the film, the complexity of the PL decay precludes a definitive interpretation of the data.

CONCLUSION

Our measurements show that for P3HT in a good solvent (100% toluene) the PL is due to intra-chain singlet excitons with a natural radiative lifetime of 1.2 ns, which is consistent with a fully-allowed transition. We have explored the effect of solvent environment on the photophysics of P3HT and find that as the proportion of poor solvent is increased, there is a substantial red-shift of absorption and PL spectra, and a dramatic drop in PL quantum yield. In a poor solvent mixture of P3HT in 17% toluene/83% methanol the absorption spectrum, PL spectrum and PL quantum yield are similar to those of the thin film, suggesting that there is a similar environment in both cases. These results show that it is possible to use solvent mixture to tune from well-solvated to film-like environments.

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