# Analysis of the excited states of regioregular polythiophene P3HT

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Poly(3-hexylthiophene) (P3HT) [90–93% regioregular,  $M_w \sim 55$  kDa, PDI <2] is studied by transient absorption spectroscopy and the properties of excited state P3HT in solution and thin film contrasted. In solution, excitation of P3HT yields the first singlet state which has a characteristic lifetime of  $\sim 600$ ps, and a measured high quantum yield of fluorescence in chlorobenzene solution of  $0.33 \pm 0.07$ . The long lived ( $\sim \mu s$ ) species in solution is ascribed to the P3HT triplet state, formed by intersystem crossing from the singlet state with a lifetime of around 300 ns in aerated chlorobenzene solution. By contrast the properties of P3HT in the solid state are very different to that in solution. The quantum yield of fluorescence is found to be reduced to only  $0.02 \pm 0.001$  and transient absorption data show the presence of two species in P3HT on a  $\sim$ 500 ps timescale, one with a lifetime of less than 500 ps and the other a longer lived nanosecond time region decay which follows a bimolecular recombination pattern. Alongside the different kinetics, both short and long lived species also show contrasting transient absorption spectra and therefore are assigned to two different species in P3HT thought to be the singlet emissive state of P3HT and charged species/polaron state respectively. Analysis of the decay kinetics suggest that P3HT singlet emissive states in the film do not decay into polaron states and therefore polaron formation must originate on earlier timescales. The competitive formation of polarons compared to emissive states in P3HT film could be exploited to generate power in organic solar cell devices more efficiently than is currently possible with donor-acceptor junction organic solar cells.

### Introduction

P3HT is an important material for current research in opto-electronic devices such as organic light emitting diodes (OLED's)<sup>1,2</sup> and field effect transistors (FET's)<sup>3,4</sup> and is the foremost material for use in organic photovoltaic polymer solar cells.<sup>5-13</sup> For application in solar cells as well as for those other applications mentioned above, a detailed understanding of the excited state behaviour of P3HT upon excitation is important to optimising device function. In particular the nature and decay behaviour of the primary excited states in P3HT is important to understand charge generation behaviour in P3HT organic solar cells. Despite the importance of P3HT as a material, a comprehensive study focussed on noting P3HT excited state properties or a general consensus on P3HT excited state behaviour is not available in the literature. In solution, P3HT, as well as many other polythiophenes, shows typical absorber-emitter behaviour with light absorption leading to population of emissive singlet states with a subsequent high photoluminescence yield (>30%).<sup>1,2,14</sup> It is this high emissive efficiency which makes these materials attractive for OLED and LASER applications. However, large differences between solution and thin film excited state character have been reported for many polythiophenes including P3HT, where the absorption in films becomes significantly red-shifted and more 'structured' showing clearer peaks and shoulders. This red-shift in absorption is nearly always associated with a large drop in

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the material photoluminescence efficiency.<sup>1,2,15–17</sup> These changes have been explained as a result of significant interactions between thiophene chains in solid films which extend the ground state conjugation across several chains providing a 2-D character to the electron-cloud delocalisation.<sup>18</sup> Similar effects have been reported for aggregation of the polymer chains in mixes of good and 'poor' solvent.<sup>15,19</sup> Some reports have shown that the addition of bulky groups to the polymer backbone<sup>1,20</sup> or by using a regiorandom instead of regioregular arrangement of side chains on the polymer backbone<sup>17,18</sup> effectively increases the separation distance between polymer chains and leads to restoration of the material properties closer to that seen in solution.

For thin films, polaron (charged species) formation in P3HT and similar polythiophenes has been reported by several groups using methods such as photoconductivity,<sup>21,22</sup> microwave conductivity,23 and transient absorption experiments.24-27 The efficiency of the polaron formation however differs greatly from report to report with values from transient absorption experiments suggesting polaron formation efficiencies of 20%+25,27 while the value from microwave conductivity measurements is only 2%.28 The relation between polaron formation and that of the neutral excited state is also not well understood as is what role polarons might play in the emissive behaviour of P3HT. Several groups have reported emission from P3HT films as from one or more intrachain or interchain excited states,<sup>29-31</sup> while in a completely different approach a recent paper has reported success in recreating the red-shifted P3HT ground state absorption and the low emission efficiency by inciting direct H-aggregate state formation in P3HT.<sup>32</sup> In this report however no explanation was given if any polaron formation was observable or even how this would be mechanistically possible.

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Here we report a systematic study of the excited states of both solution and film P3HT by transient absorption spectroscopy on  $fs_{\mu}s$  timescales as well as other optical characterisation techniques. We aim to compare and contrast the data from the two phases of P3HT to clearly resolve the species formed in P3HT films. Transient absorption spectroscopy offers an advantage in being able to observe both emissive and non-emissive species formed in the sample providing an advantage over studies which focus only on emission. Furthermore the transient data reported here for film P3HT is the first report of transient absorption on a 500 ps to several tens of nanoseconds timescale, an important timescale for observation and characterisation of short lived states in conjugated polymers such as emissive states or charged species.

## Methodology

P3HT was purchased from Rieke with a publicised regioregularity (RR) of 90–93%,  $M_w$  of 55 kDa and PDI of <2. Metal impurities were less than 0.04% Ni, 0.02% Zn and 0.04% Br. Absorption was measured using a Shimadzu UV-VIS-NIR 3100 PC spectrometer. Absorbance was not corrected for any reflection losses. Steady-state fluorescence data were measured using a Hitachi 850 fluorescence spectrometer and all spectra are corrected for equipment response.

Solution measurements except where mentioned were done in chlorobenzene open to the air at typical solution concentrations of  $\sim 4 \times 10^{-5}$  mol 1<sup>-1</sup>. Solution P3HT photoluminescence quantum yield measurements were done using the Hitachi 850 fluorescence spectrometer by comparison of P3HT in chloroform with a standard hexanol Rhodamine 6 G solution following excitation at 488 nm. In this case P3HT solution concentration was 2  $\times$  10<sup>-6</sup> mol l<sup>-1</sup> and absorbance at 488 nm was 0.01. Chloroform solution was used for this measurement rather than chlorobenzene in order to better match the refractive index of hexanol solvated Rhodamine 6 G. Time-correlated emission data for solution and film were measured using a IBH fluorocube with an LED excitation source of 408 nm. Solution transient absorption spectra on ps timescales were taken using a femtosecond transient absorption system with a 250 fs time resolution. Set up consisted of a regenerative amplifier system consisting of a 'Hurricane' Ti:Saphire laser (800 nm wavelength, 160 fs FWHM pulse width, 1.0 mJ per pulse intensity, 1 KHz repetition rate) from Spectra Physics combined with two optical parametric amplifiers (Quantronix, Topas). For a pump pulse, the output of the OPA at 476 nm at 1 KHz repetition was used as stated in the text. Laser intensity of the pump probe is given in the text. For a probe pulse in the visible region, the laser output was focused onto a sapphire plate (2 mm thick) to generate a white light continuum. The probe beam was focused at the centre of the pump beam on the sample and the transmitted probe beam then detected by an InGaAs detector after passing through a monochromator (Acton Research, SpectraPro-150). For the nanosecond transient absorption measurements light pulses from an optical parametric oscillator (OPO) system (Spectra Physics, MOPO-SL) excited by a Nd3+:YAG laser (Spectra Physics, Pro-230-10) were used for pumping light. The duration of the laser pulse was about 10 ns. A Xe flash lamp (Hamamatsu, L4642, 2 µs duration) was used as a probe source. The probe light was detected with either a Si photodiode (Hamamatsu, S-1722) for

the range 650–950 nm or an InGaAs photodiode (Hamamatsu, G3476-05) for a range 900–1500 nm after passing through a monochromator (Ritsu, Mc-10 N). Signals from the photodetectors were processed by a digital oscilloscope (Tektronix, TDS680C) before being transferred to computer. Resolution of the equipment is limited by the laser pulse length of around 10 ns.

Film samples were made by spin coating a 20 mg ml<sup>-1</sup> chlorobenzene solution at 2000 RPM for 60 seconds onto cleaned quartz slide glass. Film thickness was typically 80 nm thick and this value is used for all calculations. Photoluminescence quantum efficiency was measured using an Integrating Sphere (Hamamatsu Photonics C9920-02) following excitation at 500 nm. Sub-ns transient absorption data were taken using a custom-built transient absorption system using a 2 GHz silicon and InGaAs photodiodes (New Focus 1601 & 1611), Xenon flash lamp probe source (Hamamatsu Photonics L4642) and frequency doubled Nd-YAG laser (Ekspla SL311). During transient absorption experiments the film samples were held in a quartz cell under positive pressure of nitrogen to prevent degradation by air.

## Results

#### **P3HT** solution

Fig. 1(a) shows the absorption spectrum, emission spectrum and excitation spectrum for P3HT in solution. All spectra are corrected for equipment response. The P3HT solution spectrum is broad with a single peak at 2.72 eV (455 nm). The value at the crossing of the absorption and emission spectra is 2.25 eV (550 nm) which gives P3HT a band gap of  $\sim$ 2.3 eV in solution. The P3HT solution emission spectrum shows a peak and a shoulder at 2.12 and 1.96 eV (585 and 633 nm) respectively. The difference in energy between the peak and shoulder emission is



**Fig. 1** (a) Absorption extinction co-efficient (red line), excitation spectrum (dotted black line) and emission spectrum (green line) for 93% RR P3HT in solution at  $4 \times 10^{-5}$  mol  $1^{-1}$  concentration. Note extinction co-efficient refers to moles of the P3HT monomer unit ( $M_w$  169) (b) Absorption co-efficient (red line), excitation spectrum (dotted black line) and emission spectrum (green line) for the 93% RR P3HT film. Film thickness is ~80 nm. Excitation wavelength for emission spectra was the absorption peak maximum while excitation spectra were taken at the emission maximum. Chemical structure of the P3HT monomer is given as an inset.



Fig. 2 Transient absorption spectra for solution P3HT taken at 2 ps (top) and 14 ns (bottom) after excitation at ~450 nm. For the 2 ps spectrum laser intensity was 200  $\mu$ J cm<sup>-2</sup> incident at 476 nm and for the 14 ns spectrum laser intensity was 20  $\mu$ J cm<sup>-2</sup> incident at 455 nm.

~0.18 eV in energy and is ascribed to a C=C bond stretching frequency in the polymer.<sup>31,33</sup> Solution P3HT excitation spectra follow closely the shape of the absorption profile. The fluorescence yield of P3HT in chloroform solution was measured in comparison to a Rhodamine 6 G standard in hexanol and after adjusting for differences in the solvent refractive indexes the fluorescence quantum yield for P3HT in solution was found to be  $0.33 \pm 0.07$ . This is in good accord with literature values for P3HT or similar polythiophene polymers.<sup>2</sup>

Fig. 2 shows the transient absorption spectra for solution P3HT taken on ps and ns timescales. On ps timescales the transient spectrum is broad and shows a peak and plateau in the near IR region around 1.2 eV ( $\sim$ 1000 nm). At 14 ns the transient spectrum has narrowed significantly with an absorption peak at 1.4 eV (870 nm).

Fig. 3(a) shows a time correlated emission decay for the solution P3HT while Fig. 3(b) shows the long lived transient absorption decay on ns timescales. In Fig. 3a the P3HT singlet state emissive lifetime is found to be  $\sim$ 600 ps in good accord with literature values.<sup>34</sup> The emissive lifetime of solution P3HT was measured several times with a slight range in lifetimes which appears to correlate to solution ageing especially exposure to light. This suggests photo-degradation of the sample with time leads to some emission quenching therefore where possible fresh solutions were used in all measurements and low laser fluences. Fig. 3(b) shows the transient decay for the long-lived species in solution. The transient signal can be well fitted to a single exponential decay with a lifetime of  $\sim$ 300 ns while the transient signal amplitude is found to scale linearly with laser intensity in the range 4–20 µJ cm<sup>-2</sup>.

#### P3HT films

For ease of comparison with the solution data, the absorption, excitation and emission spectra for a thin film of P3HT spin coated from chlorobenzene solution are given in Fig. 1(b). Compared to the solution spectrum, the P3HT film absorption spectrum is highly featured and red-shifted with an absorption peak at 2.39 eV (519 nm) and shoulders at 2.23 (556 nm) and 2.05 eV (605 nm). The energy differences between peak and



Fig. 3 (a) Time correlated emission spectrum for solution P3HT measured at the emission peak following excitation at 408 nm. Prompt response is given by the grey line. The black line is a single exponential fitted to the decay with a characteristic lifetime of ~600 ps. (b) Decay for the long lived transient signal probed at 860 nm following excitation at 455 nm (20  $\mu$ J cm<sup>-2</sup> incident). The red line is a single exponential fitted to the decay with a characteristic lifetime of ~300 ns. Inset shows the transient signal scaling response to laser intensity probing at 860 nm.

shoulder, and shoulder and shoulder also roughly correspond to 0.18 eV and may also be associated with the important C=Cbond stretching frequency, however this may be coincidental. The crossover point between emission and absorbance spectra is 1.97 eV (629 nm) giving P3HT in film a band gap of  $\sim$ 2 eV roughly 300 meV smaller than P3HT in solution. The P3HT absorbance spectrum shows a low-energy tail extending up to 1.6 eV (775 nm). Incidental evidence suggests this tail in absorbance is the result of light scattering and reflectance from the sample at long wavelengths which gives a false signal in the absorbance measurements, however absorbance from sub-band gap transitions remains a possibility. Emission from P3HT in the solid state is red-shifted and much weaker than that found in solution with a shoulder 1.88 eV (650 nm) and peak at 1.70 eV (730 nm). Again the difference between peak and shoulder is 0.18 eV and can be associated with the C=C stretching frequency of the conjugated polymer backbone.<sup>31,33</sup> The intensity of the emission peaks, opposite to that seen in solution with the low energy peak being more intense than the high energy peak, has previously been explained as being due to emission from interchain (aggregate) excited states in P3HT, where symmetry considerations reduce the intensity of the high energy emission.<sup>32,35</sup> It is interesting to see that the P3HT film excitation spectrum, for the most part, resembles the P3HT absorption spectrum, however there is some obvious deviation especially at higher energies for instance at the absorption spectrum peak at 2.4 eV (520 nm). This may be an artefact of the method of measurement or the difference could reflect a true mismatch between the absorption and excitation spectra due perhaps to an intercepting intermediate state between the absorbing and emissive species. Note that the shape of



**Fig. 4** (Top) Kinetic decay for a P3HT thin film following excitation at 532 nm probing at 1.1 eV (1100 nm) as a function of laser power. Fits to the decay are an exponential plus 2nd order bimolecular decay. Light excitation was at ~ $0.5 \times 10^{15}$ ,  $2 \times 10^{15}$  and  $8 \times 10^{15}$  incident photons per cm<sup>2</sup> at 532 nm for the blue, yellow and green lines respectively. (Bottom) Transient absorption spectrum for the P3HT film taken at the system resolution of 460 ps (blue dashed line). The transient absorption spectrum is further broken down into the amplitude of the short lived decay (red) and the amplitude of the long lived decay (green).

emission spectra showed no sensitivity to excitation wavelength between 2.0 and 2.6 eV.

Fig. 4 shows the transient absorption spectra for the P3HT film measured following excitation at 532 nm. The resolution of the transient absorption equipment is 460 ps. The decay kinetics probed at 1.1 eV (1100 nm) seen in Fig. 4 (top) are biphasic with a quick system limited decay followed by a relatively slower decay. Analysis of the slow decay as a function of laser intensity reveals the decay follows a 2nd order bimolecular recombination pattern. All decays can be fitted successfully to simultaneous exponential and bimolecular decay kinetics† with a lifetime ~ 460 ps and bimolecular recombination rate  $k_{\rm bi} 3 \times 10^{11} \Delta OD^{-1}$  s<sup>-1</sup> (red lines in Fig. 4 [top]). The bottom panel of Fig. 4 shows the transient absorption spectrum obtained from the P3HT film sample measured at the system resolution of 460 ps as a function

of wavelength (blue dotted line). Analysis of the contribution from the short lived system limited decay and longer lived decay components to the total transient absorption signal as given by the fitting results are also shown in Fig. 4 bottom panel as red and green lines respectively. The short lived system limited component (red line) shows a transient absorption peak at around 1 eV or less with dwindling absorbance at higher energies. Conversely the longer lived species has a peak at 1.25 eV but has near zero absorption at lower energies where the system limited component has its absorption maximum.

#### Discussion

Analysis of the P3HT solution data appears straightforward. Light absorption by solution P3HT leads to P3HT singlet state population with a fluorescence lifetime of around 600 ps as given by the transient absorption and time resolved emission spectra. The long lifetime of the P3HT singlet excited state explains by and large the high fluorescence quantum yield from P3HT in solution of 0.33  $\pm$  0.07. From these values we estimate the radiative lifetime of P3HT in solution to be 1.8 ns, a value in good accord with the measured extinction coefficient for P3HT (of the order of 10 000 M<sup>-1</sup> cm<sup>-1</sup>). At longer times the triplet state is formed following intersystem crossing from the singlet state as confirmed by the narrowing and blue shift of the peak in the transient absorption spectrum<sup>18</sup> and the lack of any emission. This energy picture for P3HT is in good agreement with reports on other polythiophenes in solution<sup>34</sup> and an energy diagram is given in Fig. 5(A).

In contrast to solution, the data from film P3HT are very different. The data seen in Fig. 4 for the first time show without ambiguity that there are 2 species present in P3HT films at the system resolution of 460 ps and that these two states are easily discerned by their different recombination dynamics and transient absorption spectra. The short lived species responsible for the system limited decay is hard to assign due to the nature of the photodiode response and the decay kinetics not being clearly resolvable, however from the shape of the TAS spectrum which shows a peak at ~1 eV, and the known lifetime of the emissive states in P3HT (~400 ps<sup>32,36,37</sup>), we assign the system limited component to decay of emissive states in P3HT. The spectral peak for this system limited component around 1 eV is in approximately the correct position expected for S–S absorption of singlet states in conjugated polymer films<sup>25</sup> and is furthermore



**Fig. 5** Energy diagrams for P3HT in solution (A) and in film (B). For the film sample the polaron state provides a competitive pathway to emissive state formation thereby reducing the fluorescence efficiency of P3HT in films.

 $<sup>\</sup>dagger$  ΔOD =  $A_1 \exp(-t/t_1) + A_2/(1 + A_2k_{bi}t)$  where  $A_1$  and  $A_2$  are the amplitudes of each component, t is time,  $t_1$  and  $k_{bi}$  are the lifetime and bimolecular rate constants, respectively. Note  $k_{bi}$  stated is at 1.1 eV, however the value depends on probe wavelength due to changes in the polaron absorption cross section.

similar to that of the singlet state seen in solution while being slightly red-shifted, as would be expected from the increased conjugation in the solid state. The long lived decay in film P3HT however is not likely to be that of the triplet state as we find no evidence for any triplet state formation in film P3HT in accord with previous reports.<sup>18,26</sup> There is no resemblance between the transient absorption spectrum of the long lived state in the film and that of the triplet state measured in solution and furthermore the 2nd order bimolecular decay to the transient decay kinetics for the long lived species in the film suggests other than a triplet state. Previously 'polaron' charge formation has been reported following laser excitation of P3HT films and this is a better candidate for assignment to the long lived species in P3HT. Not only does the recombination of positive and negative charges mechanistically go along with a 2nd order bimolecular recombination but the TAS spectrum seen from the long lived species in P3HT also closely matches that assigned to the P3HT positive polaron in polythiophene-fullerene blend films.26 If we take the fitting results of the bimolecular recombination rate found from the TAS data,  $3 \times 10^{11} \Delta OD^{-1} s^{-1}$  and assume a molar extinction coefficient of 10 000 L mol-1 cm-1, a typical value for an absorbing chemical species, then we estimate a recombination rate of the order of  $5 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. This value is in good accord with the expected value for Langevin recombination (given a charge mobility<sup>38,39</sup> of  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and further confirms the assignment of the decay to recombination of charged species.

It is clear therefore that both neutral emissive singlet states and charged polaron species are formed following light absorption in solid film P3HT. The mechanism that leads to polaron formation is not yet well understood; however it is likely that interaction between chains in the solid state is a necessary condition for their formation as no polarons are observed in solution. Based on our observations we will begin to eliminate some potential mechanisms that could account for charge generation. Conversion of the neutral emissive states to charged species by migration to electron transfer inducing impurities in the film should be possible and could explain the low emissive efficiency of P3HT in films, however analysis of the decay kinetics suggests that this is not the case. If the singlet emissive states did undergo conversion to polarons then at wavelengths where polaron transient absorption is strong and emissive state absorption is weak, a rise following conversion of emissive states to polarons would be visible. No such rise is observed in the decay kinetics and therefore polarons are not formed following emissive state decay. Singlet-singlet annihilation to form a highly excited state that spontaneously dissociates into charged species is also potentially possible.<sup>40</sup> The data shown in Fig. 4 are actually in the annihilation regime (signal amplitude scales sublinearly with laser intensity) and therefore annihilation could account for the observed charge generation. However we note several other publications have concluded that the formation of charge species in P3HT and other polythiophene derivatives is not due to singlet-singlet annihilation but is instead a single photon process, an observation we agree with based on our own femtosecond transient absorption studies.<sup>25,27,37,41</sup> Charge generation in P3HT therefore is an intrinsic single photon process probably made possible by the strong interactions between chains in the solid state which leads to a large delocalisation of the excited state.

In Fig. 5(B) we propose an energy diagram for the excited state in solid film P3HT. As stated above polarons are not formed from the quenching of singlet emissive states and therefore we propose that polarons are formed in competition with neutral emissive states from relaxation of the initially formed excited state following absorption. The factors which govern the branching between polarons and neutral states are not yet well understood and will be the subject of forthcoming study.

In application the formation of polaron states in P3HT may be significant. The most striking difference between solution and film P3HT is the large drop in photoluminescence quantum efficiency (PLQE) from 0.33 in solution to 0.02 in film. Previously this decrease in PLQE has been ascribed to interchain/ dimer state formation<sup>1,32</sup> however an alternative explanation is also possible, namely reduction of emission as a result of efficient polaron formation following light absorption.‡To what extent polaron formation is responsible for emission quenching depends on how efficient polaron formation is. Previously polaron formation in P3HT has been suggested to be as high as 30%,<sup>25</sup> and given the low emissive efficiency of P3HT films ( $\sim 2\%$ ) then this value is more than reasonable and even has the scope to be potentially be a lot higher. From the transient data presented here we estimate the yield of polaron formation at 500 ps (given a polaron cross section of 10 000 L mol<sup>-1</sup> cm<sup>-1</sup> as above) to be at least 10%, however this may have been much greater at time zero depending on recombination. Regardless of this it is clear that polaron formation in P3HT films is not a minor product and that a value of 30% polaron formation or higher directly after light absorption is not unreasonable. Given that polaron formation is sufficiently high, then direct charge formation in films could become technologically relevant in solar cell applications. A large proportion of photon energy captured by materials in polymer-fullerene solar cells is used up in the charge generating electron transfer step at the donor-acceptor interface. Organic materials like P3HT which show intrinsic charge generation without the need for a donor-acceptor interface could therefore negate this loss mechanism and lead to greater device efficiencies, provided of course a suitable way for separating the hole and electron charges from the material before recombination could be achieved. At the time of writing already one working photovoltaic device has been reported to work on this principle.41

#### Conclusions

93% regioregular P3HT purchased from Rieke has been studied by transient absorption spectroscopy and the properties of excited state P3HT in solution and thin film contrasted. In solution, the primary excited state of P3HT is the first singlet state as confirmed by the broad transient absorption spectrum with a peak at around 1.2 eV. The singlet state has a lifetime of ~600 ps in solution, the long lifetime explaining the high measured quantum yield of fluorescence for P3HT in solution of  $0.33 \pm 0.07$ . The long-lived species in solution is ascribed to the triplet state formed by intersystem crossing from the singlet state and shows a narrower transient absorption spectrum with a peak at 1.45 eV compared to the singlet state. By contrast the

<sup>&</sup>lt;sup>‡</sup> Some loss in PLQE from a weakly emissive singlet state however will also contribute to PLQE reduction in films.

properties of the P3HT thin film are very different to that in solution. The quantum yield of fluorescence is found to be  $0.02 \pm$ 0.001 in films while the transient absorption data show the presence of two species in P3HT on a 500 ps timescale. The system limited decay is assigned to neutral-emissive state absorption in accord with the broad transient absorption only slightly red-shifted from that in solution with a peak  $\sim 1 \text{ eV}$  while the long lived decay is assigned to polaron states in P3HT. The polaron pairs recombine following 2nd order kinetics with a bimolecular rate constant 5  $\times$  10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup> (given a cross section for positive polarons of  $\sim 10\ 000\ M^{-1}\ cm^{-1}$ ). Polaron formation in P3HT is thought to be a single photon process with polaron formation competing directly with neutral emissive state formation in the film. Polaron formation therefore is partly responsible for the loss in emission yield in film P3HT and is a likely cause in emission efficiency losses for OLED's. For organic solar cells the significant formation of polarons intrinsically within P3HT may be beneficial as a way to produce electrical charges without the need for a donor-acceptor interface.

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