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Phosphorescence and spin-dependent exciton formation in conjugated polymers

Anna Köhler *, Joanne Wilson

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Abstract

The mechanism for the formation of singlet and triplet states in conjugated polymer-based light-emitting diodes (LEDs) is crucial in determining the overall efficiencies of these devices. If simple spin statistics apply then singlets and triplets should be formed in the ratio 25:75. However, the non-emissive nature of triplet states in these materials, as well as other loss mechanisms within the devices, mean that this ratio is not straightforward to measure. Nevertheless, recent experimental advances have made it possible to determine many of the properties of triplet states. Here we review what is now known about triplet states and their photophysics in conjugated polymers. We place particular emphasis on measurements of the singlet generation fraction in LEDs, and discuss the experimental techniques that have been used, such as direct comparison of photoluminescence and electroluminescence efficiencies, triplet absorption cross section measurements and magnetic resonance measurements. All of these techniques give values for the singlet generation fraction in polymers that are significantly larger than the 25% expected, and many of them have also shown that in shorter oligomers this value decreases to be closer to 25%. We also give a brief overview of recent theories for the processes of singlet and triplet formation in polymer devices.

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1. Singlet and triplet states in conjugated polymers

Commercial and scientific interest in electroluminescent conjugated polymers over the past decade has resulted in the production of efficient organic light-emitting diodes (LEDs) that are now becoming an attractive and inexpensive alternative to those based on conventional inorganic luminescent materials [1]. Commercial polymer LEDs can now operate at about 20 lm/W [2], which is more efficient than typical tungsten lamps. However, in order to advance the emission properties of this relatively new class of materials, a few fundamental issues must still be addressed and eventually resolved, and one of these is the role of triplet excited states in polymer LEDs.

In order to investigate the triplet excited states in conjugated polymers it is important to understand the differences in the formation and decay processes for these states compared to those of singlet excited states. When a conjugated polymer is in an excited state, one electron is placed in the lowest unoccupied molecular orbital and a second electron is removed from the highest occupied molecular orbital so that these two orbitals each have one electron in them. The relative spins of these two electrons determine the overall spin of

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* Corresponding author. Fax: +44-1223-353397.
E-mail address: ak10007@cam.ac.uk (A. Köhler).

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the excited state. In a singlet state the two spins are antiparallel (and precessing in antiphase) so that the total spin of the system is zero. If the two spins are parallel (or antiparallel but precessing in phase) then the overall spin is one and, as there are three degenerate ways in which this can occur, the excited state is a triplet [3]. Emission to the singlet ground state is allowed from the singlet excited state (and termed fluorescence) but forbidden from the triplet excited state due to spin selection rules. However triplet state emission can become partially allowed when a perturbation, such as spin-orbit coupling, mixes nearby singlet and triplet states. Such emission from a nominal triplet state is called phosphorescence, and it is typically long lived [3].

A triplet state can be formed directly by electrical excitation or, indirectly, by optical excitation as outlined in Fig. 1. Since optical transitions between the singlet ground state and the triplet excited state are forbidden, optical excitation of conjugated polymers initially creates only singlet excited states. Some triplet states may then be formed as a result of intersystem crossing from the singlet excited state [4–7]. The rate of this intersystem crossing is controlled by the relative energies of the lowest excited singlet state S_1, and the closest energy triplet state T_n from which it is possible to have internal conversion to the lowest triplet excited state T_1. In oligomers, the intersystem crossing rate can be a function of chain length, as a shift in the relative energies of S_1 and T_n can occur [5]. The triplet states formed via intersystem crossing from S_1 are generally non-emissive in conjugated polymers and therefore result in a reduction in the photoluminescence (PL) efficiency. Intersystem crossing can be enhanced strongly by heavy atom induced spin-orbit coupling or weakly by suitable vibrational coupling such as ring twists [5].

In contrast to optical excitation, the process of electrical excitation involves placing electrons on or removing them from polymer chains, and an electron and a hole on a polymer chain (negative and positive polarons) can recombine to form either a singlet or a triplet state. If singlet and triplet states were formed with equal cross sections then statistically 75% of injected charges would be in the threefold degenerate non-emissive triplet state while only 25% would be in the emissive singlet excited state [1]. In addition, intersystem crossing from the singlet to the triplet states can still occur. These formation ratios place a significant constraint on the ultimate efficiency with which light can be generated in conjugated polymer LEDs.

The non-emissive nature of triplet states means that they are not straightforward to investigate. In contrast to emission from the singlet state, the emission from triplet states is always extremely

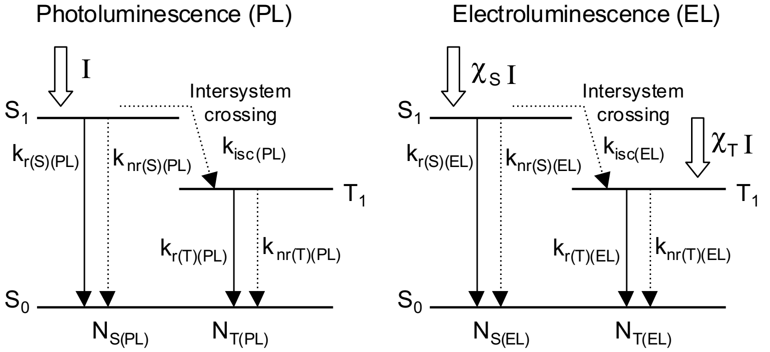

Fig. 1. Schematic diagram showing the formation and decay of singlet and triplet excited states in a conjugated polymer under both optical and electrical excitation. k_r, k_{nr} and k_{isc} denote the radiative, non-radiative and intersystem crossing rates, respectively. χ_S and χ_T refer to the fractions of singlet and triplet excitons generated, and N denotes the number of photons emitted. Reproduced from [36].

weak in hydrocarbon materials such as conjugated polymers. The spin-forbidden nature of the T_1–S_0 transition implies that the radiative decay rate does not usually compete well with the non-radiative decay [7–10]. However, thanks to the development of techniques such as time-resolved detection [8–10], optically detected magnetic resonance [11], electron paramagnetic resonance [12], pulse radiolysis and energy transfer measurements [13,14] and the substitution of heavy metal atoms into the conjugated polymer backbone [15,16] as well as the presence of some heavy metal catalyst [17] there has recently been a lot of work on triplet states that were previously inaccessible in both photoluminescence and electroluminescence measurements. Using time-resolved detection it has been possible to directly measure the triplet emission spectrum as shown for a polyfluorene in Fig. 2.

As a result of these developments, much more is now known about the energy levels and dynamics of triplets. One of the major observations has been that there is a finite, and apparently quite material-independent, S_1–T_1 energy gap (exchange energy) in conjugated polymers of around 0.7 eV, which should prevent back transfer from T_1 to S_1 [8,10,13–16]. This energy gap increases for oligomers as the singlet exciton is confined [8,14–16], but is the same in both organic [16] and organometallic conjugated polymers [15], and is independent of the amount of conjugation on the repeat unit. If the S_1–T_1 energy gap is known, it is therefore possible to estimate the energy of the non-emissive triplet states purely from the energy of the emissive singlet.

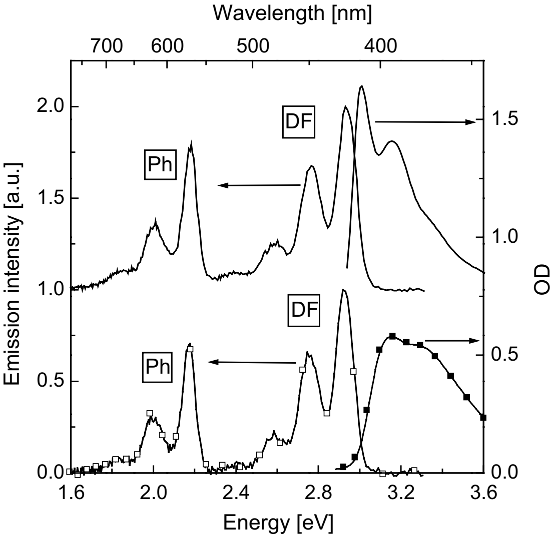

Fig. 2. Delayed emission and absorption spectra measured from the polyfluorene PF2/6 using a gated detection technique. The phosphorescence band and delayed fluorescence band are indicated by Ph and DF, respectively. Top: in MTHF at 80 K. Bottom: in a thin film at 80 K. Reproduced from [10].

2. Determining the singlet generation fraction in LEDs

In organic LEDs, the externally measured efficiency of singlet electroluminescence, η_{EL} (the number of photons emitted per electron injected), is reduced compared the fluorescence efficiency within the device structure, η_{FL}. This is due to the fact that only a fraction γ of the injected electrons and holes will combine to form excitons, only a fraction χ_S of these excitons will be in the emissive singlet state, and only a fraction η_{out} of the light will be able to couple out of the device.

$$\eta_{EL} = \eta_{FL}\gamma\chi_S\eta_{out} \tag{1}$$

The fluorescence efficiencies of the latest generation of conjugated polymers are now greater than 50% [18] and γ can tend to its limiting value of one in device architectures where electrons and holes are prevented from leaving the device if they have not recombined [19]. Light outcoupling can also be improved by patterning polymer films [20], texturing the top surface [21], designing devices with low refractive index layers [22] or by using microlenses [23] or microspheres [24]. This leaves the singlet generation fraction χ_S of only 25% as a major factor limiting the efficiency of fluorescent organic LEDs. It is therefore essential to know exactly how many emissive singlet states and non-emissive triplet states there are and what controls their formation. Several approaches have been made to determine the fraction of singlet states that are formed when an LED is operated. We now give an overview of the methods that have been used.

2.1. Comparison of absolute photoluminescence and electroluminescence efficiencies

A major discovery a few years ago was that higher numbers of singlet excitons appear to be generated upon electrical excitation of conjugated polymers than would be expected from the 25% statistical limit [1]. The first measurements which gave singlet generation fractions of at least 35–50% [19,25,26] were made by directly comparing the external electroluminescence (EL) and photoluminescence efficiencies of very efficient LEDs. Cao and coworkers [25] performed both optical and electrical measurements on the same device in an integrating sphere [27]. Ho et al. fabricated green LEDs containing a poly(*p*-phenylene vinylene) derivative for which they measured high external EL efficiencies of 6% in the forward configuration. They then determined the internal EL efficiency to be at least 15–20% by modelling the effects that the photonic structure of the LED has on the relative efficiency of radiative decay and its coupling to external radiation modes [19,26]. In the experiments of both Cao et al. and Ho et al., the devices were found to have higher EL efficiencies than would be expected from the measured PL efficiencies according to Eq. (1) if only 25% of the excitons created were in the singlet state. We note that the singlet generation fraction of 35–45% derived from the measurements of Ho et al. is a conservative estimate and it represents a lower limit to the value in this material. (Non-radiative losses at the cathode and anode have not been taken into account and γ was taken to be its maximum possible value of 1.) The photon outcoupling efficiency was computed to be 30–40% using an experimentally determined dipole distribution and recombination zone position, and an electrodynamic model that recognises the significant role of the cathode in redistributing the photon modes [26]. These calculations have subsequently been confirmed by full photon mode calculations employing the complete optical structure of the device [1] and also by Wasey and coworkers [29]. Recently, polymer LEDs with even higher external quantum efficiencies of approximately 10% have been reported [30]. These results are for different polymer systems to those discussed above, and are even more indicative that the 25% singlet generation limit may be broken, yet a detailed analysis of these devices would be needed in order to confirm this.

The drawbacks of this direct approach are that the derived singlet generation fraction is critically dependent on the accurate determination of the EL, PL and outcoupling efficiencies, and that the devices measured must have very high EL efficiencies. For the technique used by Cao et al. [25] it is also necessary to ensure that if the recombination zones are different for optical and electrical excitation, then this does not have a significant effect on the measured PL and EL efficiencies. The strength of this approach lies in the fact that the measurements are reasonably straightforward and are made on working LEDs.

2.2. Triplet absorption cross section measurements

Another approach for calculating the singlet generation fraction in conjugated polymer LEDs has been developed by Dhoot et al. [31,32] Their method is based on separately obtaining the rate of singlet formation, g_S, and the rate of triplet formation, g_T. The fraction of singlets generated is then given by

$$\chi_S = \frac{g_S}{g_S + g_T} \tag{2}$$

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[1] Full photon mode calculations have been performed in the framework of the Chance–Prock–Silbey model [28] on the basis of an ensemble of radiating in-plane dipoles embedded in the multilayered device structure and having the observed spectral distribution. The refractive index dispersion and anisotropy of all the layers, together with the radiative and intrinsic non-radiative lifetimes of the emitter are appropriately handled in these calculations.The calculations have been shown to be equivalent to quantum level calculations. The results confirm that the simple first-order treatment of [26] captures the essential physics of the problem, and provides the correct values for the photon outcoupling ratio for those devices studied.

Firstly, the rate of formation of singlets in the LED is established by measuring the external EL efficiency and also the PL efficiency (using the integrating sphere technique [27]). The outcoupling from the device is modelled, taking into account interference effects, as with the previous method. Secondly, in order to determine the rate of formation of triplets in the LED, the intensity and lifetime of photoinduced absorption from the lowest triplet state, T_1, to a higher-lying triplet state T_n are measured, as shown for a polyfluorene polymer in Fig. 3. The signal is the fractional change in transmission, $\Delta T/T$, of the sample. Using a value for the T_1–T_n absorption cross section (estimated on the basis of pulsed radiolysis measurements and quantum chemical calculations) along with the T_1 lifetime from photoinduced absorption measurements, it is possible to obtain a rate for triplet formation [31]. Photoinduced absorption spectra can contain contributions from both the $T_1 - T_n$ absorption and absorptions associated with the polaron states formed by charges in conjugated polymers as a result of strong structural and electronic relaxation in the excited state. However, it is fairly straightforward to separate the required T_1–T_n absorption from that due to the polarons since the signals will have different lifetimes and temperature dependences.

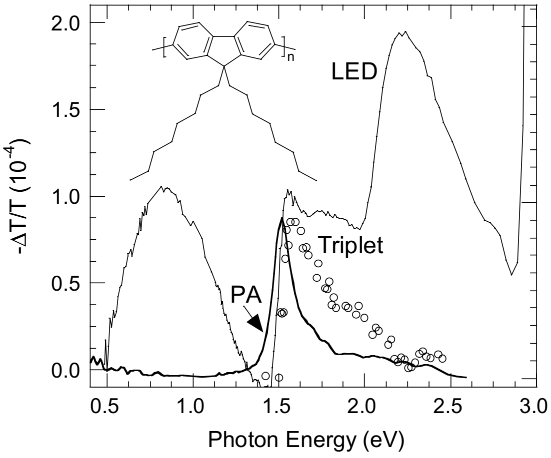

Fig. 3. The photoinduced absorption spectrum of poly(9,9-dioctylfluorene) measured in a device with Au and Ca/Au electrodes, recorded at 90 K and 13.3 Hz (thin line). The polymer thickness is 50 nm and the current density is 9.2 mA/cm^2. The triplet signal extracted by phase analysis is shown as circles, and the thick line is the photoinduced absorption spectrum for a 100 nm thick poly(9,9-dioctylfluorene) film illuminated with 20 mW of laser excitation at 351 and 361 nm at 80 K and 125 Hz. The chemical structure of poly(9,9-dioctylfluorene) is shown in the inset. Reproduced from [32].

The singlet and triplet formation rates are then combined to obtain the singlet generation fraction which was found to be greater than 50% in the case of poly(9,9-dioctylfluorene) [32] and greater than 80% in the cases of a poly(*p*-phenylene vinylene) derivative [31] and poly(9,9-dioctylfluorene-co-benzothiadiazole) [32]. All of these values were seen to be independent of the drive voltage.

In contrast to the previous method, this approach does not require very high EL efficiencies, so it may be applied to a wide range of conjugated polymers within working device structures. However it is a complex technique that also depends on accurate determination of PL, EL and outcoupling efficiencies. In addition, an accurate value for the T_1–T_n absorption cross section is essential. Nevertheless, the value for χ_S obtained for poly(9,9-dioctylfluorene) with this technique agrees with that found using a different method [31–34].

2.3. Magnetic resonance measurements

A combination of photoinduced absorption and optically detected magnetic resonance measurements may also be used to obtain the ratio of cross sections for singlet formation, σ_S, and triplet formation, σ_T, and to derive a singlet generation fraction χ_S from this according to Eq. (3) [33–35].

$$\chi_S = \frac{\sigma_S}{\sigma_S + 3\sigma_T} \tag{3}$$

These measurements are made on thin films rather than working LEDs. In the photoinduced absorption measurement, the polaron P_1 and P_2 absorption peaks are monitored and, if necessary, the sample is photooxidised to obtain larger polaron signals. These polaron levels are then split into spin up and spin down sublevels by the application of a magnetic field. Spin up and spin down polarons decay with different rates depending on whether they form polaron pairs with an overall parallel or antiparallel spin. A chopped microwave absorption is then used to pump the system to equilibrium, so that both spin up and spin down polaron levels are populated equally again. From the intensity of this absorption signal (which is a change in ΔT and denoted δt), Wohlgenannt and co-workers determine the ratio of cross sections for the formation of singlet and triplet states [35]. They found that this ratio varies over quite a range and is always greater than the value of 1 expected for equal formation cross sections. Their results are shown in Fig. 4, where the experimentally determined ratios of formation cross sections are plotted as a function of the polaron energy and inverse chain length.

The advantage of this technique is that it can be applied to so many different materials that the dependence of the singlet generation fraction on material properties can be monitored. The main disadvantages are that the measurements are not made on working LEDs, and that photooxidation is sometimes used to enhance the signal, which may change the properties of the materials.

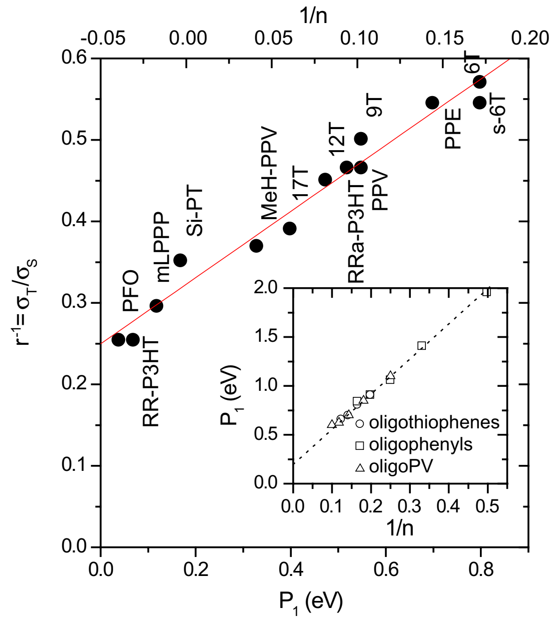

Fig. 4. The ratio $r^{-1} = \sigma_T/\sigma_S$ of spin-dependent exaction formation cross sections in various polymers and oligomers as a function of the peak photon energy of the P_1 transition. r^{-1} is also shown as a function of the inverse conjugation length $1/n$, which was determined from P_1 by linear extrapolation (see inset). The line through the data points is a linear fit. The inset shows the peak photon energy of the low energy polaron transition, P_1 in slightly oxidized oligomers as a function of the inverse conjugation length (CL). The number n denotes a CL that corresponds to an oligothiophene with n rings. Reproduced from [33].

2.4. Compounds with both fluorescence and phosphorescence

An alternative method for obtaining the singlet generation fraction that does not require measurement of the absolute PL and EL efficiencies or outcoupling efficiency is to use materials that exhibit emission from both the singlet and triplet states such as the platinum-containing polymer and monomer shown in Fig. 5 [36].

The emission from the triplet state is obtained by introducing strong spin-orbit coupling through the incorporation of heavy platinum atoms in the polymer and monomer backbones. Conjugation is preserved through the metal sites as a result of mixing between the frontier orbitals of the metal and the conjugated ligands [37]. The only difference between optically and electrically exciting the compounds should be the extra triplets that are directly formed with electrical excitation, as can be seen when comparing the EL and PL spectra of an LED at 10 K in Fig. 6.

The number of singlet and triplet excitons generated is calculated from the number of fluo-

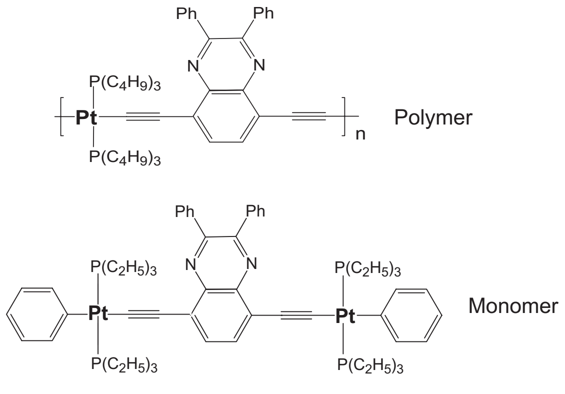

Fig. 5. Chemical structures of the Pt-containing polymer and its corresponding monomer used to measure both fluorescence and phosphorescence in electroluminescence and photoluminescence. Reproduced from [36].

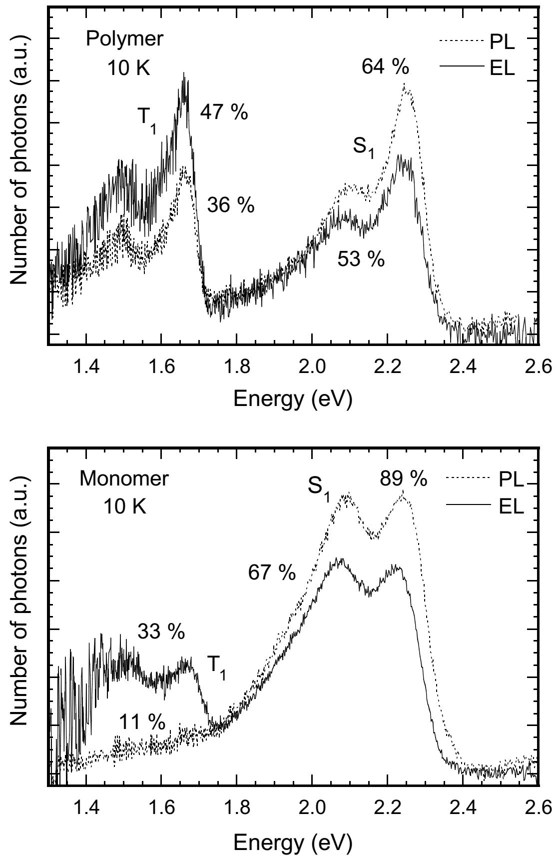

Fig. 6. Comparison of the photoluminescence spectra (dotted lines) and electroluminescence spectra (solid lines) of light-emitting diodes at 10 K for (a) the platinum-containing polymer and (b) the monomer. The triplet emission is denoted by T_1 and the singlet emission by S_1. The spectra have been plotted in terms of the number of photons and the fraction of the total emission that the singlet and triplet emission represent are given as percentages.

rescence and phosphorescence photons emitted by considering the radiative and non-radiative decay paths as shown in Fig. 1 and described in [36]. For electrical excitation of these compounds the ratio of the number of photons emitted from the triplet state to the number of photons emitted from the singlet state, R_{EL}, can be directly measured from the electroluminescence spectrum. The equivalent ratio, R_{PL}, for optical excitation can then be obtained from the photoluminescence spectrum. Comparison of these two ratios results in a value for the singlet generation fraction χ_{S}

$$\chi_{\mathrm{S}} = \frac{R_{\mathrm{PL}}}{R_{\mathrm{EL}}} \tag{4}$$

This calculation assumes that the intersystem crossing rate is the same for electroluminescence and photoluminescence, and that the radiative and non-radiative decay rates for singlet and triplet excited states are the same for EL and PL. These assumptions were tested by using pulsed optical and electrical excitation to obtain emission decay times. In addition, the measured singlet generation factions did not vary with electric field strength or optical excitation intensity over the working ranges of the devices.

The singlet generation fractions obtained for the polymer and monomer are shown in Fig. 7 as a function of the temperature of the devices. A significant difference can be seen between the singlet generation fractions obtained for the polymer and monomer of the same material. The monomer's singlet generation fraction is close to the 25% expected from simple spin-statistics, but that of the polymer is around 50% [36].

The main advantage of this method is that it involves a relative measurement, and many factors cancel out in the determination of the singlet generation fraction. It is not necessary to create very efficient devices or to model the outcoupling

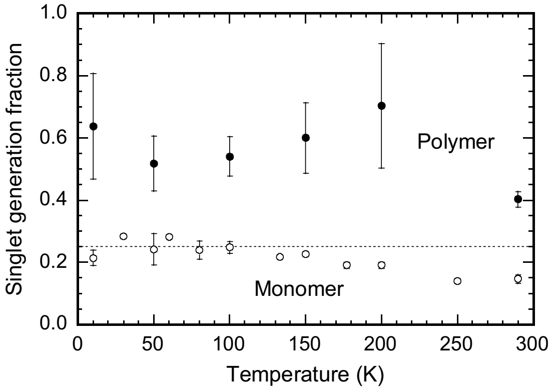

Fig. 7. The singlet generation fraction χ_{S} for the platinum-containing polymer and monomer plotted as a function of temperature. The error bars on each point represent the statistical error obtained by measuring a large number of devices. The dotted line represents the fraction (0.25) expected from simple spin statistics. Reproduced from [36].

or the triplet absorption cross section. The effect of spin-orbit coupling is taken into account quantitatively in both PL and EL through the intersystem crossing rate from S_1 to T_1 and the triplet decay rates, so that the singlet generation fraction is accurately determined. In fact a conceptually similar technique was used by Baldo et al. [38] to determine a singlet generation fraction of 22 ± 3% in the small molecule Alq_3. By blending Alq_3 with both fluorescent and phosphorescent dopants it was possible to detect both singlet and triplet emission in the photoluminescence and electroluminescence spectra. Then, by comparing the relative intensities of singlet and triplet emission in PL and EL and determining the efficiency of energy transfer to the dopants, the singlet generation fraction could be obtained. The obvious disadvantage of this technique is that it can only be used on specific systems that show both fluorescence and phosphorescence and which therefore usually have strong spin-orbit coupling induced by the presence of heavy atoms. In addition, the effect of strong spin-orbit coupling on the singlet generation fraction itself is not exactly clear.

2.5. Summary of experimental results

The LED based measurements [19,25,31,32] for hydrocarbon conjugated polymers all agree on singlet generation fractions that are well above 25% statistical limit. This is in contrast to measurements by Baldo et al. on the metal-containing molecule Alq_3 where a singlet generation fraction of 22 ± 3% was found [38]. In measurements on a Pt-containing polymer and its corresponding monomer very different singlet generation fractions were found for the two materials [36]. The singlet generation fraction in the polymer was around 50%, as seen for hydrocarbon conjugated polymers, while that in the monomer was only about 22%, in agreement with the measurements on Alq_3. This suggests that a spin-dependent recombination mechanism is at work in polymers that favours singlet state formation so that the statistical limit of 25% no longer applies. In contrast, it appears that spin-independent recombination still occurs for molecules and that this produces 25% singlets as expected. In addition, recent work by Wohlgenannt et al. has demonstrated a dependence of the singlet generation fraction on oligomer length and on the energies of the polaron absorptions (which are in turn related to the effective conjugation lengths) for a wide range of materials [33].

3. Reasons for spin-dependent exciton formation

The various experiments outlined above have shown that for conjugated polymers, the formation of excited states appears to be spin-dependent. We now address the issue of what is actually controlling the fractions of singlet and triplet states that are generated. Several different suggestions have been put forward so far [4,5,33,34,39–43] and, while there is no clear answer yet, it has emerged that there are two requirements for spin-dependent exciton formation. The first is that there must be different rates for forming the singlet and triplet states. The second is that there must be a mechanism for randomising the spins if an excited state has not been formed within a given time from an electron and hole that are in close proximity to one another. For example, two charges that have arrived on a polymer chain could jump off onto different chains before they have had time to form a bound state on the first [36]. Alternatively, the electron and hole could form an intermediate charge transfer (CT) state that has negligible exchange energy and allows intersystem crossing between the singlet and triplet manifolds prior to the formation of bound singlet or triplet states [43,44]. Consequently, if the formation rate is higher for one of the final states then it is more likely to be formed before the randomising process occurs, and is therefore formed more frequently.

There are many possibilities for why such a difference in formation rates between singlets and triplets could exist that have been considered by both experimentalists and theoreticians, and a number of these are outlined below. One view is that the formation rate is influenced by the energy difference between the original polaron states present on a conjugated segment and the singlet and triplet states to be formed. The dissipation of energy into the vibrations of the lattice on formation of singlet and triplet states would favour the formation of singlets [4,41,43,45], since the S_1 singlet state is closer in energy to the original polarons than the triplet state. This is essentially a Marcus theory argument which takes into account the vibrational relaxation from the polaron levels into singlet and triplet states. (When comparing this model with experimental data it is important to note that the separation between S_1 and T_1 energy levels in a range of conjugated polymers has been seen to be similar [16].) Furthermore, Bittner and Karabunarliev demonstrate the role of an intermediate charge transfer state in this process. They show how a conjugation-length-dependence of the energies of the lowest singlet and triplet excitonic states with respect to this charge transfer state should result in variations of the singlet generation fraction [43].

In contrast, Hong and Meng consider a two step process which consists firstly of the spin-independent formation of a singlet and a higher-lying triplet T_2 state, and secondly of the vibrational relaxation from this T_2 state to the lowest T_1 triplet state [39]. The authors consider that the transition from T_2 to T_1 is a phonon cascade process so, if the T_2–T_1 energy is large, then there will be a bottleneck in the T_2–T_1 non-radiative transition and intersystem crossing from T_2 to the singlet manifold will be favoured which increases the singlet yield. Back transfer from T_1 to S_1 is also considered. There are some slight complications with this scheme that are discussed by Tandon et al. [42]

A conceptually different approach developed by Tandon et al. [42] compares the energies and the ionic or covalent character of the states to be formed with the energy and the ionic character of the initial polaron pair [34,42]. The formation rate then depends on the wavefunction overlap between the initial polaron pair and final singlet and triplet states. Since the singlet S_1 state has a more ionic character than the triplet T_1 state, this should therefore result in a high singlet generation rate. This is further assisted by the smaller energy gap between the initial polaron pair and the final singlet state compared to the triplet state. In this model the chain length dependence of the singlet generation fraction is accounted for by the different evolution of singlet and triplet state energies with oligomer length. Theoretical dependences of the singlet generation fraction on the applied electric field and the presence of nitrogen heteroatoms were also examined.

A similar model to this developed by Shuai et al. and later extended by Ye et al. also finds a higher formation rate for the more ionic singlet state than for the triplet state which has more of a covalent character [40,46]. These authors show that the formation rates for singlet and triplet excitons are affected by intermolecular charge transfer and recombination processes, which have contributions from both the interchain one electron transfer matrix elements (the probability of jumping from one chain to the next) and the two electron bond charge integrals (the electron repulsion between electron density around a bond on one chain and a site on an adjacent chain). They also show that for a constant ratio of interchain transfer matrix element to bond charge integral, there is an increase in the ratio of singlet to triplet formation cross sections with increasing conjugation length [46]. The differences between the models of Shuai, Ye and coworkers and Tandon and coworkers are discussed in detail in [42].

It has also been suggested that exciton formation may occur from an intermolecular charge transfer state either directly into the lowest S_1 and T_1 states or via some higher-lying singlet S_n or triplet T_n state which then relaxes vibronically though the singlet or triplet manifolds to the lowest S_1 and T_1 states [44]. The limiting step here is considered to be the formation of the S_n or S_1 states rather than the vibrational relaxation. A chain-length-dependence of the formation rate arises from the reduction of the energy gap between the CT state and the S_1 state with increasing chain length. For short oligomers, the CT–S_1 gap is large and charge recombination occurs through the higher-lying singlet and triplet excited states. As these states have similar cross sections, the singlet generation fraction is close to 25%. In contrast, for long oligomers the CT–S_1 separation is smaller and the channel involving direct recombination into S_1 dominates resulting in a singlet generation fraction that can exceed the spin statistical limit.

4. Outlook

Recent research has demonstrated the importance of spin-interactions in the formation of excited states. We expect that in the near future detailed models will improve our understanding of these processes. Considering what is known at present about the formation of singlet and triplet states, there appear to be a number of ways in which the efficiency of conjugated polymer LEDs could be improved:

1. One approach would be to tailor the branching ratio between singlet and triplet states so that only emissive singlet states are produced in LEDs. From the current theories this might conceivably be achieved by either altering the energy levels of the singlet and triplet excited states with respect to the energy levels of the polarons, [4,41,43,45], by altering the character of the excited state wavefunction [34,36,40,42,46], or by altering the length of the polymer or oligomer [33,36].
2. Another approach would be to reduce the S_1–T_1 energy gap in order to allow back transfer of excitons generated in the T_1 state in LEDs to the S_1 state. Less activation energy is required for this process when the S_1–T_1 energy gap is smaller and the intersystem crossing rate should be greater. However, recent work on the S_1–T_1 energy gap in a range of conjugated polymers has shown that this energy gap is almost independent of the polymer structure [16]. Consequently, it may be very difficult to alter the S_1–T_1 energy gap for polymers unless charge-transfer states or transitions that involve orbitals with very different shapes (such as n–π^*) can be used.
3. If it were possible to make very efficient phosphorescent polymers then the formation ratio between singlets and triplets would no longer be important. Efficient phosphorescence requires a high radiative decay rate from the triplet state that competes favourably with the non-radiative decay rates caused by processes such as diffusion to dissociation sites or internal conversion [7,36]. Incorporating heavy metal atoms such as platinum in the conjugated backbone gives the necessary spin-orbit coupling for a strong radiative decay. However, even in compounds with so much additional spin-orbit coupling, the non-radiative decay rate of the triplet state on the polymer is too high for efficient phosphorescence. So although many triplet states can be produced, they decay inefficiently [7]. It may be possible to reduce the internal conversion rate by carefully tailoring the energy of the triplet state or the highest phonon mode on the conjugated backbone. Diffusion might be suppressed by incorporating heavy atoms off the main polymer backbone, and such materials are beginning to be investigated now [47].
4. The triplet energy harvesting technique that has been used so successfully in small molecule LEDs could also be applied to conjugated polymers. In order to have efficient energy transfer from the polymer to the phosphorescent dye molecules, it is important to know the energies of the triplet states in the polymers [8–10,13–15]. Some work using this technique has already been performed for conjugated polymers [48].

Whatever the future may be for this area of research, the possibility that simple spin statistics do not apply to conjugated polymers is very interesting. It also suggests that there is significant potential for improving the efficiencies of polymer LEDs.

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