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Hot band emission and energy transfer in organic electrophosphorescent devices

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Abstract

The evolution of the electroluminescence spectra of platinum porphyrin doped polyfluorene light-emitting diodes is investigated after turn-off of the driving pulse. In the delayed spectra a new emission band is identified, which is of comparable intensity to the delayed polyfluorene emission. Through temperature dependent photoluminescence measurements an assignment of this emission is made to a hot level of the platinum porphyrin with a thermal activation energy of 0.42 eV. The evolution of the delayed emission spectra as well as the observation that the hot band at 540 nm overlaps the polyfluorene triplet level suggest that energy transfer can occur between the host and guest. © 2002 Published by Elsevier Science B.V.

1. Introduction

Much effort has been directed to the understanding of the physical principles governing polymer light-emitting diodes (LEDs) [1]. Currently, the greatest puzzle relates to the role of triplet excitons [2–11]. Charge carriers injected at opposite electrodes of an LED can combine to form excitons either in the singlet or in the triplet state whereby typically only the singlet emits. Although the precise ratio of singlet to triplet excitons is debated, it appears that approximately half the excitations formed are in the triplet state [2,4,7,11]. The interest in the triplet state of conjugated polymers has also been fed by the demonstration of efficient triplet harvesting and emission from phosphorescent dopants [10,12,13]. Whereas in some blend systems triplet energy transfer is observed, in others charge trapping dominates, resulting in direct recombination on the guest dopant [10,13,14]. For polyfluorene doped with 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP) it has been shown that – at low excitation densities – charge trapping dominates over energy transfer [10,13]. Previous studies have focused on steady state measurements and spectrally integrated time resolved EL measurements. We present here for the first time both spectrally and temporally resolved EL measurements, which reveal an array of interesting dynamical emission features.

2. Experimental

The polymer studied is a blue-emitting polyfluorene, poly(2,7-(9,9-bis(2-ethylhexyl)fluorene))

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(PF2/6). PF2/6 solutions were doped with different concentrations of the red phosphor PtOEP. LEDs were fabricated on solution etched indium tin oxide (ITO) substrates ultrasonicated in isopropanol. An injection layer (50 nm) of poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate was deposited on the ITO and dried on a hot plate. The spincoated PF2/6 films were contacted with 15 nm thick calcium electrodes, 4 mm^2 in area, covered with aluminium (150 nm) and subsequently mounted in a water cooled cold finger cryostat under rotary pump vacuum. Fig. 1 shows the structures of polymer and dopant. EL spectra were measured under pulsed excitation with 50 μs pulse length, duty cycles of 10% and typical biases of 4–5 V. The spectra were recorded by an EG&G intensified gated diode array coupled to a 0.3 m monochromator with 150 lines/mm grating and variable entrance slit width. Two material configurations are compared in the following. The first system is a 1% (w/w) blend of PtOEP (Porphyrin Products) in PF2/6 (referred to as the heavily doped device), the second, referred to as the lightly doped film, contains approximately 0.001% by weight PtOEP in PF2/6 in order to give a known time delayed signature, and is considered to be identical to a neat film. Photoluminescence (PL) measurements were performed in vacuum under excitation by a frequency-doubled mode-locked titanium–sapphire laser. Temperature dependent PL measurements were performed in a continuous flow helium cryostat.

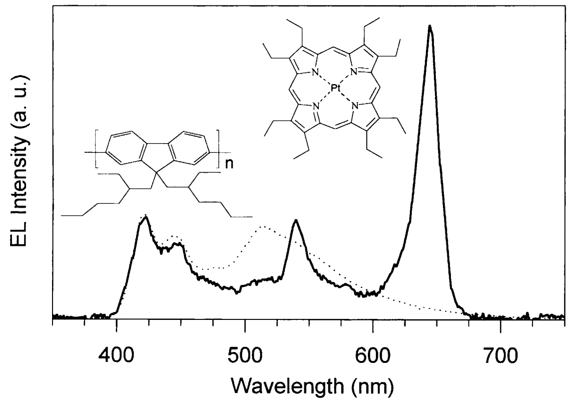

Fig. 1. Cw spectrum of a lightly platinum porphyrin (PtOEP) doped polyfluorene (PF2/6) LED (dashed line) compared to the delayed emission spectrum of a heavily doped PF2/6 LED (solid line) measured through a 600 nm short-pass filter with an integration window of 40 μs, 1 μs after turning off the device. The insets show the structures of PF2/6 and PtOEP.

3. Results

Fig. 1 shows a cw spectrum (dotted line) of the lightly doped PF2/6 LED. It displays the typical vibronic bands at 420, 445 and 475 nm as well as a broad, featureless band around 520 nm, which is commonly observed in polyfluorenes [13,15] and will be referred to as a defect band. The solid line shows a spectrum of the heavily doped device obtained 1 μs after the end of the voltage pulse, integrated for 40 μs. As PtOEP has an emissive lifetime in the order of tens of μs, the delayed emission is dominated by the red porphyrin emission. In order to detect any residual host emission, the delayed luminescence was recorded through a 600 nm short-pass filter (see Fig. 5) in all cases, which reduces the intensity of the PtOEP peak by approx. 10^{-3}. Three main features are seen in the delayed emission spectrum of the heavily doped device. The blue emission is identical to the cw spectrum of the lightly doped device, but falls off faster to longer wavelengths, indicating a reduction in the defect band due to trapping [15]. A new, narrow feature appears at 540 nm, which shall be the focus of the subsequent investigation.

Fig. 2a shows the change of emission intensity with time for the doped sample, recorded in 4 μs time windows. Both the porphyrin peak and the new feature at 540 nm decay exponentially with a lifetime of 22 μs, whereas the host emission decays strongly non-exponentially. The 540 nm peak of the delayed spectra was corrected for the host defect band as discussed below. The decay of the porphyrin and PF2/6 peaks is contrasted in Fig. 2b for both devices. The decay of PtOEP is similar for both devices, with a small increase in lifetime on this time-scale to approximately 40 μs in the lightly doped device. However, the decay of the blue host emission is very different for the lightly doped device and does not exhibit the rapid reduction in intensity seen in the heavily doped device. The inset in Fig. 2b shows the decay of the emission

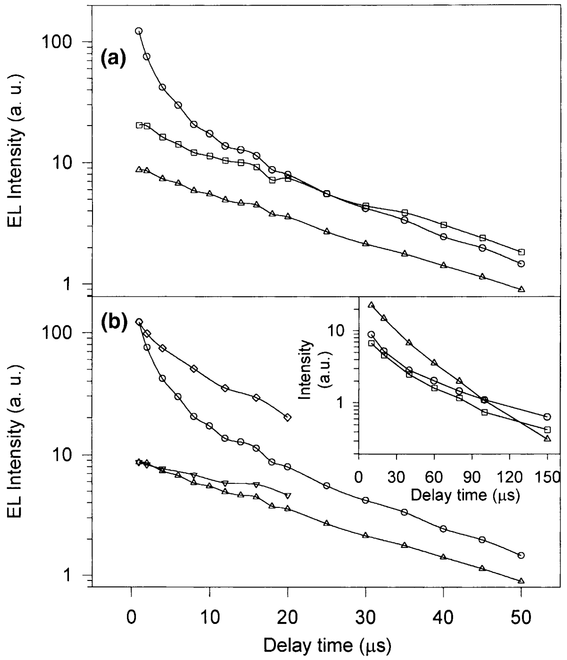

Fig. 2. (a) Decay of the three emission peaks of a PF2/6 LED doped with 1 % PtOEP (heavily doped device), integrated for 4 μs: blue host emission band at 430 nm (◯), green emission band at 540 nm (□), red guest emission at 650 nm (△). (b) Comparison of the decay of host and guest emission for both devices (the symbols for the heavily doped device are as in panel (a)): lightly doped device host emission at 430 nm (◇), guest emission at 650 nm (▽). Inset: decay of the heavily doped device EL on longer time-scales, detected in 40 μs windows. The lines are a guide to the eye. Note that the decays were measured through a short-pass filter. The individual traces in the main figure are offset for clarity and therefore do not indicate absolute peak ratios.

maxima on longer time-scales, integrated for 40 μs. Here the new band at 540 nm decays like the host emission, and not like the PtOEP emission, as is observed within the first 50 μs. The PtOEP lifetime increases to 36 μs. The long-scale PtOEP lifetime in the lightly doped device (not shown) is found to be 51 μs, in agreement with previous data [13].

The decay dynamics are very different for the strongly and lightly doped devices. In order to identify the origin of this difference we studied the luminescence decay as a function of temperature. Fig. 3 contrasts the temperature dependence of the delayed emission (20 μs delay, 40 μs window) for the two device configurations, with the emission normalised to the blue host peak. In order to measure the delayed spectra, the entrance slit of the detector was opened in this case, corresponding to a reduced spectral resolution of 10 nm. Whereas there is little dependence on temperature for the lightly doped device, for the heavily doped device the new peak at 540 nm is found to increase with a concomitant decrease in red PtOEP emission with increasing temperature. The cw spectra (not shown) show a small increase in the broad defect emission at 520 nm with increasing temperature and a decrease in PtOEP emission relative to the blue host emission similar to that observed in the delayed spectra of the heavily doped device. The inset in Fig. 3 shows the room temperature PtOEP to PF2/6 peak emission ratios plotted as a function of delay time. Whereas the peak ratio for the heavily doped device changes by over a factor of 5 with time and exhibits a clear maximum, the peak ratio for the lightly doped device is close to constant. This shows that the PF2/6 emission obeys very different decay kinetics in the lightly and heavily doped device with respect to the direct phosphorescence from PtOEP.

It has recently been shown that gated EL spectroscopy can be employed as a technique to distinguish between delayed emission resulting from uncorrelated charge carrier pairs and neutral long-lived excitations by applying a small bias offset to the device [16]. Also, gated spectroscopy allows the identification of different trapping sites contributing to the emission, as different sites give rise to different characteristic time constants in the emission. In the present case these techniques provide evidence that the PtOEP red emission peak and the new emission feature at 540 nm are not fully correlated. In Fig. 4a the room temperature delayed EL spectra of the heavily doped device are plotted for different delay times. As the delay increases, the blue and the green band both increase with respect to the PtOEP emission, although at short times, as seen from Fig. 2a, the decay of the 650 and 540 nm peaks is identical. As the new 540 nm band is overlapped by the 520 nm defect emission, it is not possible to deduce the exact ratio of the emission components due to the low spectral resolution employed. As the delay time increases, a slight blue-shift of the 540 nm band is observed due to an

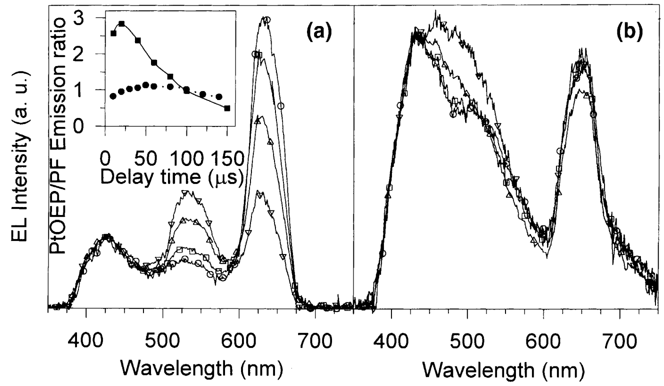

Fig. 3. Gated emission spectra of lightly and heavily doped PF2/6:PtOEP LEDs at 263 K (○), 283 K (□), 303 K (△) and 323 K (▽) detected 20 μs after switch-off through an entrance slit corresponding to a spectral resolution of 10 nm, integrated for 40 μs. (a) Heavily doped device emission detected through a 600 nm short-pass filter; (b) lightly doped device emission. Inset: temporal evolution of the guest to host emission peak ratio in heavily (■) and lightly (●) doped LEDs.

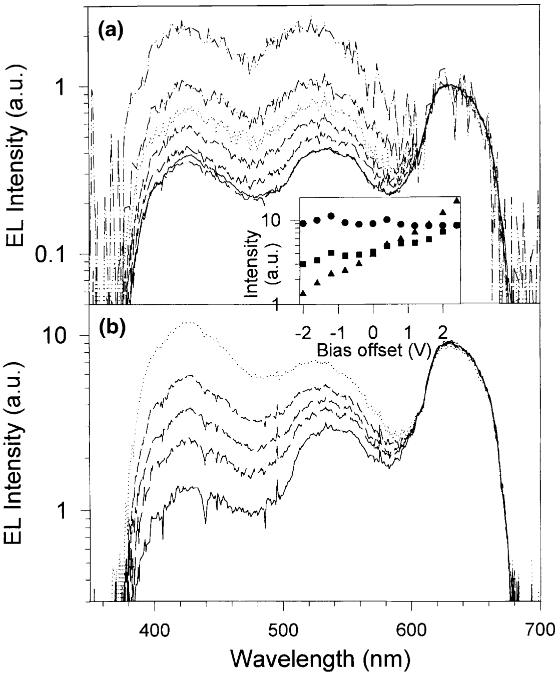

Fig. 4. (a) Delayed EL spectra of the heavily doped device integrated for 40 μs, normalised to the guest emission peak, detected at delays of 10, 20, 40, 60, 80, 100, and 150 μs (from bottom to top). (b) Change of delayed EL spectra (30 μs delay, 40 μs integration) with bias offset for −2, −1.2, 0, 1.2, 2 V (from bottom to top). Inset: plot of intensity at 430 nm (▲), 540 nm (■) and 650 nm (●) as a function of bias offset.

increase in weighting of the defect band with respect to the 540 nm band. As the defect emission component is reduced in the delayed spectra [16] one obtains a lower estimate of the 540 nm emission intensity by subtracting the defect component of the cw spectra, as was done for the data in Fig. 2. It is important to note that the 540 nm emission, although having an identical decay to the PtOEP within the first 50 μs, decays more slowly than the PtOEP peak at longer times. At very long delay times of up to 400 μs the three peaks could be detected without the need of a red filter, demonstrating that the blue and green peaks are indeed much longer lived than the red phosphorescence. This observation also ties in with the dependence of the delayed emission spectra on bias offset shown in Fig. 4b. For this measurement, a bias offset was applied to the LED driving pulse and the amplitude was kept at a constant value. The peak intensities are plotted as a function of bias offset in the inset of Fig. 4 and show a dramatic dependence of delayed host emission on bias offset, whereas the PtOEP emission is virtually not affected. Although it is hard to distinguish between the 520 nm defect band and the 540 nm band in detail, it appears that the 540 nm band is reduced for negative bias offsets and enhanced for positive bias offsets, whereas the main PtOEP band is not. This demonstrates that the 540 and 650 nm bands do have different activation pathways post turn-off.

In order to determine the origin of the 540 nm band we performed cw PL measurements on PtOEP doped polystyrene films. Fig. 5 shows the absorption and PL spectra (detected through the short-pass filter, excited at 390 nm) and the transmission spectrum of the filter used. Evidently the novel peak is a characteristic of PtOEP rather than of polyfluorene. The 540 nm band is clearly seen in PL together with a vibronic feature at 580 nm. No change in the relative peak intensities was observed upon variation of the laser excitation wavelength around the Sorret band from 360 to 410 nm. Both peaks were found to be very sensitive to ambient oxygen and decreased at an identical rate during purging with air. The 540 and 580 nm emission is mirrored exactly in the absorption. The Stokes' shift is 184 cm^{-1} and the separation between the main band and the side band is 1280 cm^{-1} in absorption and PL. The high energy PL peak is strongly thermally activated, as shown in the inset of Fig. 5. The activation energy is 0.42 eV, which compares to the separation of the main PtOEP emission peak and the activated side band (0.39 eV). The inset also shows the relative ratios of the two PtOEP peaks in the delayed EL at 10, 30 and 80 μs delay, normalised to the ratio at 323 K. The activation of the 540 nm emission peak in the case of EL is non-Arrhenius and considerably weaker than in PL, and deviates increasingly strongly from the PL activation with increasing delay time.

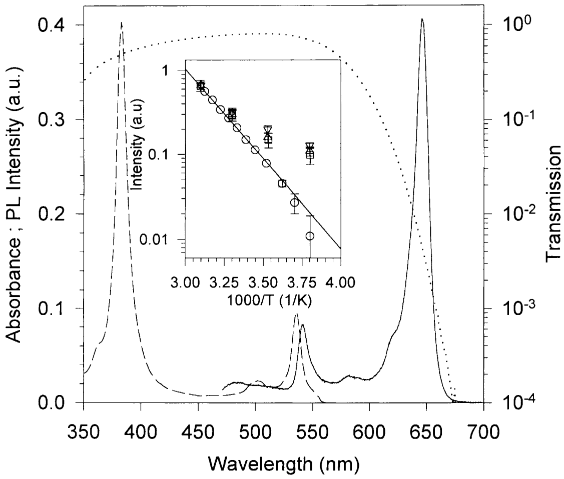

Fig. 5. Plot of absorption (- - -) and steady state filtered PL (–) spectra of a PtOEP doped polystyrene film. The dotted line shows the transmission of the filter used to detect the hot band in the PL. The inset shows the thermal activation of the hot band at 540 nm in PL (○) and in EL detected at 10 μs (□), 40 μs (△) and 80 μs (▽) delay. The solid line indicates an activation energy of 0.42 eV, corresponding to the splitting between the two bands. Note that the hot band is over three orders of magnitude weaker in intensity than the main phosphorescence band.

4. Discussion

Our observation of a new narrow band in the delayed EL spectra, which is of similar intensity to the delayed host emission, is surprising. It is particularly noteworthy that this new feature is very similar in shape and position to the phosphorescence band of PF2/6 previously reported [8], and coincides energetically exactly with the triplet energy of polyfluorene as determined by pulse radiolysis [5]. However, the temporal decay of the 540 nm peak within the first 50 μs is identical to that of the 650 nm porphyrin peak and the same peak occurs in the PtOEP PL, demonstrating that the novel feature is an intrinsic property of PtOEP. Such an emission, narrowly offset from the absorption (Stokes' shift of 90 cm^{-1}), has been observed in phosphorous porphyrins [17] and has been attributed to $Q(0,0)$ fluorescence. Thermal activation of the $Q(0,0)$ emission, referred to as hot band emission, has previously been observed in a number of metalloporphins [19]. The electronic nature of the new excited state at 540 nm is rather puzzling and will have to be investigated in greater depth. We note that the thermal activation of the band with an energy corresponding to the offset from the $T(0,0)$ level is characteristic of emission from a higher lying excited state. However, due to the likelihood of internal conversion this is very improbable for a long-lived triplet state. In contrast, the PtOEP singlet at 585 nm is very short lived (≈ 70 ps) and has a very low quantum yield [18]. Time resolved PL measurements on PtOEP using a streak camera setup showed no decay of the 540 nm band on the scale of 2 ns, suggesting that it is not due to singlet emission. It is also conceivable that the 540 nm emission is actually short lived but appears long lived in PL and EL due to a slow populating mechanism.

Photoinduced absorption measurements have previously demonstrated that triplets are not transferred from the polyfluorene host to the PtOEP dopant at low temperatures [13]. The present measurements are in general agreement with this, as the initial decay of both PtOEP bands is singly exponential and does not indicate immediate triplet transfer post turn-off. However, there are a number of important observations to be made. Firstly, on longer time-scales the 540 nm emission follows the delayed host emission, not the guest emission (Fig. 2). As the delay time is increased, the 540 nm emission increases with respect to the main PtOEP band (Fig. 4). Secondly, the application of a bias offset modifies the delayed host and 540 nm bands, but not the main PtOEP band (Fig. 4). This demonstrates that the delayed 650 nm PtOEP emission is due to phosphorescence excited during the voltage pulse and not due to delayed carrier recombination. Thirdly, the thermal activation of the 540 nm peak in EL is non-Arrhenius, and deviates increasingly from the PL activation with increasing delay time of the detection window (Fig. 5). All of these observations point to a further populating mechanism of the 540 nm band, which is independent of the main $T(0,0)$ level at 650 nm [18], and suggest that host triplets may transfer directly to the porphyrin hot band.

We also note that the delayed emission properties of both guest and host differ for the strongly and weakly doped systems. There are three important observations: firstly, the 650 nm PtOEP emission decreases with respect to the host emission of the heavily doped device in both cw and gated detection as the temperature is increased (Fig. 3). For the lightly doped device there is no significant reduction in phosphorescence with respect to delayed host emission with increasing temperature. Secondly, the host decay kinetics are very different for both devices as evidenced by the comparison in Fig. 2 and the inset in Fig. 3. Thirdly, the guest lifetime decreases with increasing concentration. Lane et al. [13] found no dependence of EL lifetime on concentration, however, their devices were excited with extremely high pulses of 70 V, which may modify the decay dynamics. Although it is not clear whether the 540 nm band is due to a singlet or a triplet, it does appear that an interaction between guest and host triplets can take place. This influences the decay lifetimes, the temperature dependence and the host singlet emission due to triplet–triplet annihilation [6,9] and can provide a further understanding of the dependence of device efficiency [10,13] on concentration, polymer host material and temperature.

5. Conclusions

We have demonstrated gated spectroscopy of an electrophosphorescent polymer LED. The technique is highly sensitive and can map out delayed emission components over 1000 times weaker than the cw luminescence. A narrow novel emission feature is identified in the delayed spectra after most of the host emission has decayed. Temperature dependent PL of PtOEP unambiguously leads to the identification of this feature, which is attributed to a thermally activated ‘hot’ band. This band may be used as a microscopic temperature probe of organic optoelectronic systems and could provide a sensitive alternative method to frequency up-conversion for studying thermal effects in LEDs [20]. The results suggest that hot bands are important in triplet energy transfer processes in LEDs and should be taken into account when designing phosphors for both endothermic and exothermic triplet conversions [21].

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