

BMB-2T: m.p. 261 °C; MS: *m/e* 662 (M^+); $^1\text{H-NMR}$ (600 MHz, chloroform-*d*₁) σ (ppm): 7.38 (2H, d, $J = 3.7$), 7.34 (2H, d, $J = 3.7$), 6.82 (8H, s), 2.30 (12H, s), 2.13 (24H, s). Elemental Analysis: Calc. for $\text{C}_{44}\text{H}_{48}\text{B}_2\text{S}_2$: C, 79.76; H, 7.30; B, 3.26; S, 9.68. Found: C, 79.62; H, 7.38; S, 9.68.

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Harvesting Singlet and Triplet Energy in Polymer LEDs**

By Vicki Cleave, Goghan Yahiolu, Pierre Le Barny, Richard H. Friend, and Nir Tessler*

Molecular semiconductors now demonstrate excellent performance as the emissive materials in light-emitting diodes (LEDs).^[1,2] An important reason for this is their high luminescence efficiency; this is due to the strong binding between the electron and hole produced by either optical or electrical excitation, causing formation of neutral bound states, termed excitons.^[3,4] Because these excitons are strongly confined, the relative spin configuration of the spin- $\frac{1}{2}$ electron and spin- $\frac{1}{2}$ hole influences the binding energy, the spin-triplet being lower in energy than the spin-singlet by the exchange energy. Radiative decay from singlets is fast (fluorescence), but from triplets is spin-forbidden (phosphorescence) and often very inefficient. Whilst

photoexcitation directly produces singlet excitons, operation of LEDs brings together electron and hole from opposite electrodes, and, statistically, should generate triplets and singlets in the ratio 3:1.^[5] Where triplet radiative decay is not possible, LEDs are limited to 25 % efficiency (for 100 % efficiency of singlet emission). Triplet emission is partially allowed in the presence of spin–orbit coupling, and is seen in molecular semiconductors in which elements of high atomic number are present. The use of triplet emitters to improve LED efficiency has already been proposed.^[6]

We present here a study of LEDs in which platinum octaethylporphyrin (PtOEP) is used as a “dopant” in a semiconducting polymer host. This material is known to be an efficient triplet emitter in the solid state, with emission in the red part of the spectrum (645 nm), and we show that it can be efficiently excited in these LEDs. By time-resolved measurements of light emission, we are able to show that this arises by capture at the PtOEP of both singlet and triplet excitons formed in the polymer host. These results demonstrate the feasibility of surpassing the efficiency limit set by spin statistics and achieving very efficient molecular LEDs.

Dye dopants are widely used to control color and to improve efficiency of organic semiconductor LEDs.^[7,8] Such dopants can be excited by energy transfer from singlet excitons generated in the host via Förster energy transfer,^[9] or may function as traps for either electron and hole, and thus act as recombination centers. Recently it was shown^[10,11] that the acceptor molecule could also be a triplet-emitting PtOEP.^[12,13] Forrest et al.^[10] use the small molecule aluminum tris(8-hydroxyquinoline) (Alq3) as host; we use the polymer poly[4-(*N*-4-vinylbenzyloxyethyl, *N*-methyldi-*N*-(2,5-di-*tert*-butylphenyl)naphthalimide)] (PNP). Under conditions where the PtOEP is emissive, the host triplet energy must lie higher, and triplet emission from the PtOEP can arise from up to three excitation mechanisms: i) singlet exciton transfer from the host by Förster transfer, ii) triplet exciton transfer from the host by Dexter transfer, and iii), electron–hole capture at the PtOEP. If channels (ii) or (iii) are active, this allows extra conversion efficiency, which is not possible from singlet excitons alone.

For Förster and Dexter^[14] energy transfer to work simultaneously, the energy levels of both singlet and triplet in the host have to lie above the corresponding levels in the guest. Moreover, efficient transfer requires an overlap of emission in the host and absorption in the guest.^[9,14,15] While Förster transfer can be easily achieved, it may be less trivial to satisfy simultaneously the requirements for an efficient Dexter transfer. Since data on the energy position of the triplet state are not available for most light-emitting polymers, the procedure for finding a proper system involves trial and error. Figure 1 describes the host–guest combination that we found to allow both Förster and Dexter energy transfer. Figure 1a describes the chemical structure of PNP (host) and PtOEP (guest). Figure 1b shows the absorption and photoluminescence (PL) spectra of the two compounds. To test in-

[*] Dr. N. Tessler, V. Cleave, Prof. R. H. Friend
Cavendish Laboratory, Cambridge University
Madingley Road, Cambridge, CB3 0HE (UK)

Dr. G. Yahiolu
Chemistry Department
Imperial College of Science, Technology and Medicine
Exhibition Road, South Kensington, London SW7 2AY (UK)

Dr. P. Le Barny
Thomson-CSF
Domaine de Corbeville, F-91404 Orsay (France)

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dependently the Förster energy transfer we first used optical excitation, which generates only singlets^[15] in the host. As shown in Figure 1b the good overlap between the absorption of the singlet Q-band in the porphyrin (550 nm) and the emission from the polymer fulfills the main requirement for Förster energy transfer from the singlet state in the host to the singlet state in the porphyrin. The presence of the heavy metal (platinum) in the porphyrin then ensures fast intersystem crossing (ISC) to the triplet state in the PtOEP molecule and subsequent emission from this state. In order to test the efficiency of the Förster energy transfer, films consisting of blends of 0.1 %, 0.5 %, and 1 % by weight of PtOEP in PNP were made and excited optically (Fig. 2). At 1 %, there is complete energy transfer to the guest, as expected for the relatively long-range dipole–dipole Förster coupling. We also measured the absolute luminescence efficiencies,^[16] and find that these track with the concentration of PtOEP: the pure PNP shows 72 % yield (excitation at 457.9 nm), and 5 wt.-% blends of PtOEP in PNP and in poly(methylmethacrylate) were found to have yields of 29 %, and 26 %, respectively (excitation at 457.9 nm and 514.5 nm, respectively). These measurements indicate almost complete energy transfer from the singlet on PNP to the triplet on PtOEP.

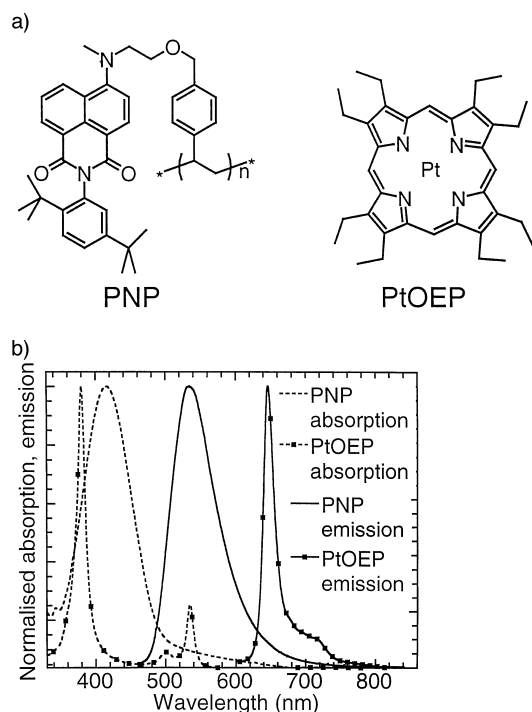


Fig. 1. a) Chemical structure of the host polymer PNP and the guest molecule PtOEP. b) Emission and absorption spectra of films of the two compounds. Emission from PtOEP was measured for a sample consisting of 5 wt.-% PtOEP in poly(methylmethacrylate). Excitation was at 457.9 nm for PNP and 514.5 nm for PtOEP.

We used the PNP/PtOEP blends as emissive layers in LED structures, which were based on those found to operate well for the host PNP, with the general structure indium tin oxide / polyvinylcarbazole / PNP / calcium.^[17] We drive these diodes with short voltage pulses, using techniques re-

ported elsewhere,^[18] and time-resolve the emitted light. For diodes made with undoped PNP we observe a prompt response, as is shown in Figure 3, whereby the bulk of the emission has decayed within 1 μ s. The emission spectrum (not shown here) is similar to the photoluminescence spectrum shown in Figure 1b. The diodes made with the doped PNP show similar efficiencies but very different characteristics in other respects. We have chosen to work with low concentrations of the PtOEP and present results for the 0.1 % blend. At this low concentration we see emission from both host and dopant, and the comparison between the two provides a convenient internal calibration. Furthermore, we were anxious to minimize changes to the diode electrical characteristics due to the presence of the dopant, since addition of dopants is known to affect the injection balance and/or position of the recombination zone in LEDs.^[17]

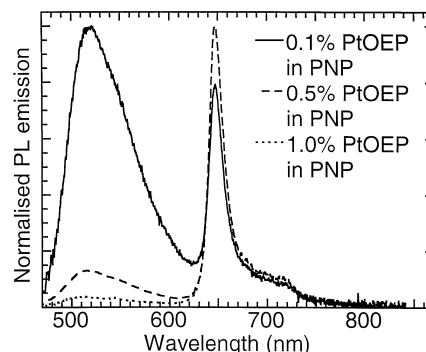


Fig. 2. Photoluminescence spectrum of films made of 0.1 wt.-% (full line), 0.5 wt.-% (dashed line), and 1 wt.-% (dotted line) of PtOEP in PNP. The excitation wavelength was 457.9 nm, at which wavelength the absorption of the host (PNP) is much stronger than that of the guest (PtOEP). Film thicknesses were typically 80 nm.

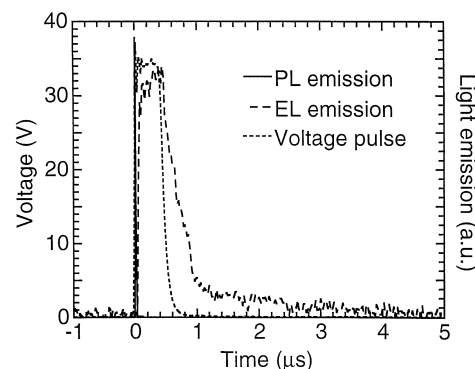


Fig. 3. Temporal response of luminescence of PNP (0 % PtOEP) under optical and electrical excitation. Photoexcitation was with ~ 0.2 ps laser pulses at 355 nm, and the short response shown (solid line) is limited by the photomultiplier response (< 20 ns). Pulsed electrical excitation was made with a 400 ns duration 25 V pulse. The electrical excitation setup and the LED structure [18] had an RC time constant less than 20 ns. The electroluminescence shows a double exponential decay of 340 ns and 1.7 μ s. The structure of the LEDs consisted of indium tin oxide on glass as hole-injecting electrode, onto which 60 nm of poly(9-vinylcarbazole) (PVK) as hole transport layer and 60 nm of PNP as electron transport/emissive layer were sequentially spin coated. The top electron contact consisted of ~ 200 nm Ca, covered in ~ 200 nm Al. Under CW drive conditions these LEDs showed an external quantum efficiency (emission from all angles) of about 0.5 %.

Figure 4a shows the photoluminescence (PL), and continuous wave (CW) electroluminescence (EL) spectra of the 0.1 % blend. This clearly shows that the ratio between the triplet and singlet emission is larger in the LED by almost a factor of two. In an LED one must also account for spectrally dependent interference effects^[19] caused by the metal electrode. Assuming the guest and host dipoles have similar position and orientation we can make use of the emission spectrum of the PNP as a reference to correct for this effect (dashed line). Using this correction we find that there is still 40 % more dopant emission in the LED compared with the optically excited films. This suggests that indeed there is an extra source of energy for the triplet emission under electrical excitation, which we consider is due to capture of triplet excitons formed in the PNP at the PtOEP sites.

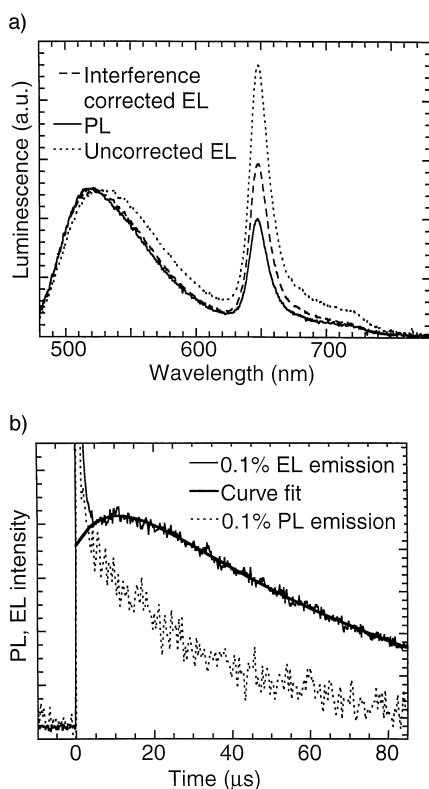


Fig. 4. a) Normalized photoluminescence (solid line, bottom) and electroluminescence (dotted line, top) spectra of 0.1 % PtOEP in PNP. The dashed line is the electroluminescence spectrum corrected for interference effects induced by the metallic contact. The structure of the LEDs is as described in the caption to Figure 3, except that the PNP is blended here with PtOEP. All LEDs were tested under vacuum conditions. b) Time evolution of light emission from optically and electrically excited 0.1 % PtOEP in PNP films. Both responses show a peak at $t = 0$ (unresolved), resulting from the PNP singlet emission, followed by a slower response of the PtOEP. Excitation conditions are as described in the caption to Figure 3. The smooth line describes a fit using Equation 1, see text.

Direct evidence for the migration of triplet excitons from host PNP to guest PtOEP is provided by measurements of time-resolved emission, as shown in Figure 4b. Time-resolved emission was measured using a fast photomultiplier tube and sampling oscilloscope; the system time response is <20 ns, as shown for the (fast) singlet PL from PNP in Fig-

ure 3. When the PtOEP is present, both PL and EL show longer response times. The PL response of a 0.1 % PtOEP in PNP shows a combination of emission from both the host and guest, having short and long lifetimes, respectively. A 76 μ s lifetime is unambiguously deduced from 5 % PtOEP in PNP (not shown), where the emission is entirely from the PtOEP triplet state. The EL response is more complex; it shows a fast initial response, with a further rise over the first 10 μ s, before falling exponentially. We consider that this arises because the excitation of the PtOEP is accomplished by both the fast Förster transfer of singlets from PNP, and the slower transfer of triplets from PNP to PtOEP by Dexter transfer. While the singlet-singlet (Förster) transfer typically occurs on a nanosecond time scale,^[20–22] the triplet-triplet (Dexter) energy transfer is often on a microsecond scale.^[21,22]

It is interesting to note that the time evolution shown in the doped LED is very similar to those reported by Harri-man and co-workers,^[21,22] where simultaneous Förster and Dexter transfers were observed in a system made of DNA (donor) and a porphyrin (acceptor). Following Harri-man and co-workers methodology^[21,22] it is possible to attribute the fast initial rise to the Förster transfer and the longer rise to the Dexter mechanism. The solid line in Figure 4b shows a fit to Equation 1 for the emission rate r , where F and D are constants and τ_1 and τ_2 are time constants. τ_1 is considered to be due to the Dexter transfer and τ_2 is the PtOEP triplet emission lifetime. The fit results in $\tau_1 = 10$ μ s, $\tau_2 = 80$ μ s, and $D/F = 46$ %, which is in good agreement with the 40 % deduced independently from the emission spectra (Fig. 4a).

$$r = (F + D(1 - e^{-t/\tau_1}))e^{-t/\tau_2} \quad (1)$$

An alternative explanation for increased emission in the red may be that the porphyrin acts as a trap for carriers and hence part of the charge recombination occurs directly on the porphyrin. The long rise time would then be explained as the time it takes to capture the second type of carrier on the porphyrin. A supporting argument could be that in this case the dopants may enhance charge injection and/or device efficiency as reported elsewhere.^[17] To check whether the long rise time could be attributed to carriers remaining within the device for a long time before recombining, we repeated the time-resolved measurement but with a DC offset of -8 V. That is, as soon as the voltage pulse is off, the device is biased at -8 V and all remaining carriers are expected to be extracted on a short time scale.^[18] The reverse field, however, is not expected to affect neutral excitons such as the triplets. The result of this measurement was almost identical to the one reported in Figure 4b, showing that delayed recombination is not important. Moreover, the percentage of the additional emission in the red reported in Figure 3 was found to be independent of PtOEP concentration (0.1 %, 0.5 %, 1 %). If

traps were involved one would expect it to be more efficient in trapping drifting carriers as the concentration goes up. On the other hand, when the Förster transfer is incomplete, each porphyrin molecule is effectively independent of the others and has its own singlet capture range. Since Dexter transfer is not expected to be of larger spatial extent the same is true for capturing triplets, and hence the ratio of the two contributions is independent of the number (concentration) of porphyrin molecules.

To conclude, we have provided several experimental results that, when taken together, prove that it is possible to capture the energy from both singlet and triplet excitons and transform it into light emission. This result suggest that it should be possible to make use of 100 % of electron-hole recombination and it lifts the proposed 25 % limit on EL efficiency. Although it is not trivial to find a material combination that will support Dexter transfer as well as Förster transfer, we believe that careful material design will broaden the scope of this technique. We note that even if the porphyrin acts as a recombination center and not as a triplet scavenger, the 25 % limit can still be broken due to the efficient intersystem crossing on the porphyrin. We also showed that we can separate the contributions arising from either singlets or triplets in the host. In order to comment on the ratio between singlets and triplets as generated in the LED, the above result needs to be supplemented only by a measurement of the fraction of triplets that are actually captured by the guest. Another aspect of this work may be that shortening the triplet lifetime in the polymer blend will remove degradation channels associated with the triplet state.^[23]

Finally, we would like to comment that although the statistical ratio of 3:1 for the ratio of triplets to singlets formed under EL conditions is widely discussed in the literature, there is considerable speculation that there are spin-dependent electron-hole capture processes that lead to a lower ratio in practice. This discussion is driven by recent reports of unexpectedly high LED efficiencies, e.g., 16 lm/W and above in the green part of the spectrum.^[24,25] It is hard to measure this ratio experimentally, unless there is direct measurement of the triplet population, for example by excited state absorption.^[5] We note that our measurements of triplets through their transfer to the PtOEP provide another route to achieve this. If we assume that all triplet excitons generated in the PNP are captured at PtOEP sites, the 40 % enhancement in triplet emission for EL in contrast to PL (Fig. 4) sets the triplet:singlet production ratio as low as 0.4:1. This is very much a lower limit, since it is unlikely that all triplets are transferred to the PtOEP. Further work is in progress concerning these points.

A more complete description of the work by Forrest et al.^[10] has recently been published by Baldo et al.,^[26] showing evidence for triplet-triplet energy transfer in Alq3 and PtOEP blends.

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A Simple Colloidal Route to Planar Micropatterned Er@ZnO Amplifiers**

By Marco Kohls, Thomas Schmidt, Haymo Katschorek, Lubomir Spanhel,* Gerd Müller, Norbert Mais, Adriana Wolf, and Alfred Forchel

Erbium-doped fiber amplifiers (EDFAs) are important optical components used to recover the transmitted light signals in the third telecommunication window near

[*] Dr. L. Spanhel, M. Kohls, T. Schmidt, H. Katschorek, Prof. G. Müller
Lehrstuhl für Silicatchemie, Fakultät für Chemie und Pharmazie
Bayerische Julius-Maximilians Universität Würzburg
Röntgenring 10, D-97070 Würzburg (Germany)
N. Mais, A. Wolf, Prof. A. Forchel
Lehrstuhl für Technische Physik, Physikalisches Institut
Bayerische Julius-Maximilians Universität Würzburg
Am Hubland, D-97076 Würzburg (Germany)

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