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Förster energy transfer and control of the luminescence in blends of an orange-emitting poly(*p*-phenylenevinylene) and a red-emitting tetraphenylporphyrin

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We report on the luminescence of a tetraphenylporphyrin, TPP-d, blended into poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene], MEH-PPV. We find significant energy transfer from MEH-PPV to the porphyrin, in spite of the low absorption of the porphyrin at the emission wavelength of MEH-PPV, reflected in a Förster transfer radius (2.5 nm) smaller than for materials with larger spectral overlap. The overall photoluminescence, PL, efficiency decreases monotonically with increasing porphyrin content, whereas the porphyrin contribution to the total efficiency, referred as an "apparent" PL efficiency, exhibits a maximum at 1.4% porphyrin content (by weight). We attribute this non-monotonic behaviour to the interplay of the exciton transfer probability and PL quenching, both of which increase with concentration. We also observed the energy transfer under electrical excitation, but noticed that, at low concentrations, the porphyrin contribution to the electroluminescence is higher than that observed in PL. This indicates significant emission from excitons formed directly at the porphyrin sites, which are likely to act as charge trapping sites. We also compare the luminescence properties of the blends with those of copolymers based on the same host–guest pair.

1. Introduction

Electroluminescent polymers have been attracting much attention over the past ten years,[1] and light-emitting devices based on them have now achieved performance (efficiency, lifetime and luminance) good enough for practical applications. Achieving "pure-red" emission has proved relatively challenging, and this has stimulated research into red light-emitting polymers, as these are also required together with those emitting in the blue/green region for full colour displays. Recently, the use of porphyrins, known for a long time as red emitters, has been reported in devices based on low molecular weight organic materials[2,3] and on polymers.[4,5] The use of Pt-containing porphyrins, in order to harvest radiative decay of both singlets and triplets in light-emitting diodes, LEDs, has also been reported.[2,4]

The free base tetraphenylporphyrin (or 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine), TPP, displays saturated red fluorescence, with a 13%[6] quantum yield in benzene solution, whereas the phosphorescence was reported to be negligible,[6] owing to lack of sizeable spin–orbit coupling effects. Recently, there have been reports on the use of TPP as guest in red-emitting diodes based on either small molecules[7] or polymers,[8] which aim at exploiting energy transfer of the excitons formed in the host, to TPP, in order to achieve saturated red emission. Note that efficient energy transfer, of the Förster type,[9] ideally requires a large spectral overlap between the emission of the "donor" and the absorption of the "acceptor" species. Such efficient energy transfer was observed for instance when blending TPP with blue-emitting polymers, such as poly(9,9-dioctylfluorene), PFO,[8] owing to the large overlap of the polymer's emission with the absorption Soret band of TPP. We have previously reported on the synthesis[10] and luminescent properties[11] of copolymers based on a PPV-like backbone and on a tetraphenylporphyrin derivative, 5,10,15-tris(4-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphine, TPP-d, grafted as a side group (see Fig. 1a). These copolymers can be described as poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene], MEH-PPV, derivatives with porphyrin side groups (see Fig. 1a). In spite of the small absorption of TTP-d in the spectral range of MEH-PPV emission, we found relatively efficient energy transfer. We chose MEH-PPV because it is a well characterised polymer, which also allows fabrication of efficient LEDs.[12]

In this paper we shifted our attention to blends of the same porphyrin, TPP-d, with MEH-PPV. The use of the blending approach has several advantages over the copolymer one. Firstly, it allows easier control of the amount of porphyrin, whose incorporation in the copolymer was instead not linearly related to the feed-ratio of the copolymerisation reaction. Furthermore, the transport and luminescent properties of the MEH-PPV are expected to be affected only marginally. This is because in the case of the copolymer, the presence of the porphyrin is expected to influence the polymerisation reaction of MEH-PPV, inducing "hard-to-control" changes in the chain length and substantial disorder along the chains. In the case of the blends however, the addition of the porphyrins should only induce a modest increase in structural disorder. However, the blends have the drawback of likely long term instability due to porphyrin aggregation. The main purpose of this study is to

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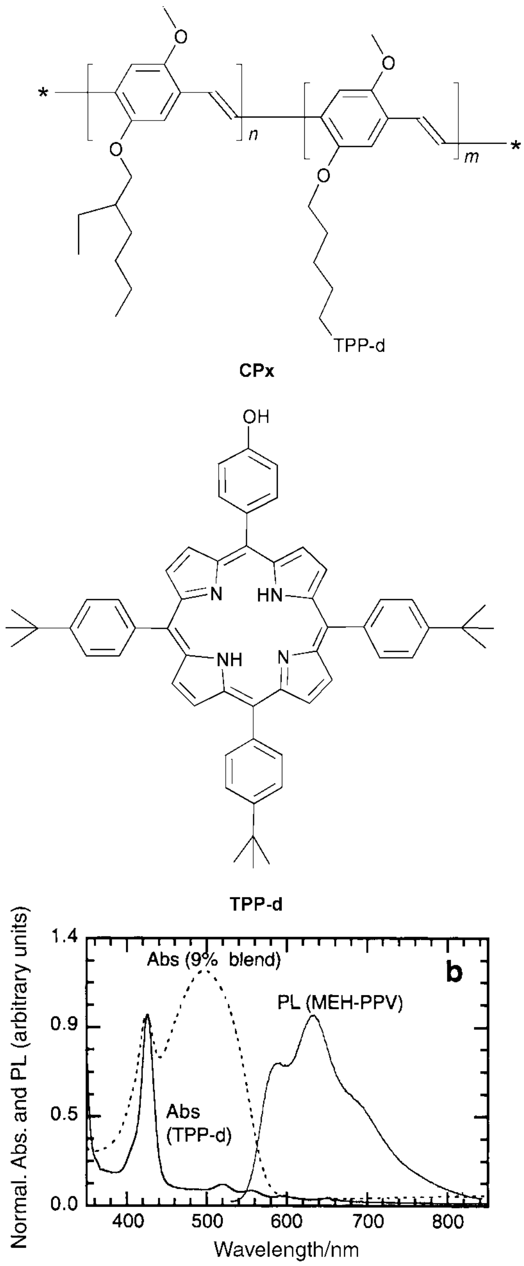

Fig. 1 a) Molecular structures of the statistical copolymers (**CP*x***, $x = 1$, 2 or 3), of MEH-PPV (with $n = 0$) and of the porphyrin chromophore, TPP-d, used in the blends. Note that the TPP-d chromophore used in the blends is the hydroxy derivative, while in the copolymers it "loses" the hydrogen establishing an ether-like bond. b) Optical absorption of TPP-d dispersed in PVK (1% by weight), and of a film of the MEH-PPV blend with 9% porphyrin, nomalized in relation to the porphyrin Soret band at 421–422 nm. The PL spectrum of a film of neat MEH-PPV is also shown. Note that the peak at ~500 nm is due to MEH-PPV and not to the porphyrins.

allow a better controlled variation of the photoluminescence (PL) and electroluminescence (EL) of these blends with the porphyrin content, in order to rationalise the results previously obtained for the copolymers, and investigate the differences between the two approaches.

2. Results

The optical absorption of the porphyrin chromophore, TPP-d, dispersed in poly(vinylcarbazole) (PVK) (1% by weight), is compared with the PL emission of an MEH-PPV film, and with the absorption of a film of the blend (9% weight of TPP-d) in Fig. 1b.

The PL emission of MEH-PPV:TPP-d blends is shown in Fig. 2a. The porphyrin emission is well identified by the two peaks at about 660–661 nm and 716 nm, corresponding to the so-called Q(0,0) and Q(0,1) transitions, respectively, from singlet excited states. As expected, the porphyrin contribution to the total emission increases with the porphyrin content, although it may seem surprising that similar contributions to the total emission by the porphyrin and the MEH-PPV are observed with a porphyrin content as low as 0.34%. The MEH-PPV emission is almost completely quenched for the 9% blend. These results show that there is significant energy transfer from the MEH-PPV to the porphyrin chromophores, in spite of the low absorption of the porphyrin. The PL efficiency of the neat MEH-PPV is ~19%, whereas that of the blends decreases monotonically with porphyrin content, reaching a value of 4.4% for the 9% blend (Fig. 2b). The continuous decrease in the efficiency of the blends suggests the existence of porphyrin induced exciton quenching. We note that the reported value for the PL efficiency of TPP is about 13%,[6] and that we measured a similar value, of ~12.5%, for blends of TPP-d in PVK with low porphyrin content (up to 2.6%, by weight). In this case we used an excitation beam at 325 nm, which is absorbed by both systems (PVK and porphyrin), but mainly by the PVK. A "complete" Förster energy transfer, from PVK to the porphyrin, is inferred from lack of detectable emission from the PVK. This is not unexpected, however, in view of the large overlap of the PVK emission (peaking at ~400 nm) and the Soret band of the porphyrin (at about 421 nm). At higher porphyrin contents (blends with 4.6% and 9.0% porphyrin) there is a significant decrease of the PL efficiency, which we attribute to concentration quenching effects.

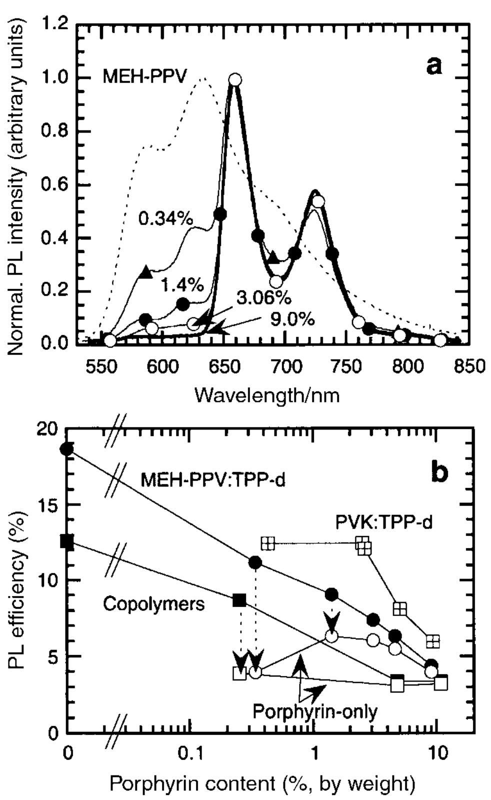

Fig. 2 a) PL spectra of MEH-PPV and films of some of the blends. b) PL efficiency for the PVK:TPP-d and MEH-PPV:TPP-d blends and for the copolymers. The "apparent" PL efficiency of the porphyrin in the MEH-PPV:TPP-d blends (open circles) and in the copolymers (open squares) is also shown. The arrows are guides to the eye.

In Fig. 2b, we also report the PL efficiency calculated considering only the porphyrin contribution to the emission of the MEH-PPV:porphyrin blends. This porphyrin "apparent" PL efficiency was calculated by multiplying the porphyrin contribution to the overall PL spectra of the blends (ratio of the area of the porphyrin PL spectrum to the area of the overall spectrum) by the overall PL efficiency. Note that this corresponds to the ratio of photons emitted by the porphyrins divided by the number of total exciting photons, and not the ratio of the photons emitted by the TPP-d divided by the excitons transferred to the TPP-d, which is the true efficiency of the porphyrin in that environment. This "apparent" efficiency is increasing with porphyrin content at low concentrations, it reaches a maximum for the 1.4% weight blend, and decreases for the higher concentrations. The decrease also corresponds to the decrease of the PL efficiency of the blends in a PVK matrix.

It is interesting that the PL efficiency of the copolymers also decreases with increasing amount of porphyrin (see Fig. 2b). Incidentally, we note that the MEH-PPV used in the blends comes from a different preparation batch from the MEH-PPV used in the copolymers study[10] and has higher PL efficiency. This is consistent with the observation that the efficiency of the blends is always higher than that of the copolymers. These differences are also reflected in the electro-optical characteristics of the corresponding light-emitting diodes.

Fig. 3 shows how the porphyrin contribution to the total emission increases with the porphyrin content, and this can be used to fine tune the emission colour by tuning of the chemical dopant concentration.

Fig. 4 shows the characteristics of LEDs prepared with these blends as active layers sandwiched between a PEDOT:PSS hole-transporting layer and calcium cathodes [PEDOT = poly(3,4-ethylenedioxythiophene) and PSS = poly(styrene-sulfonate)]. The current, luminance and EL efficiency decrease with increasing amount of porphyrin. As shown in Fig. 4b, the turn-on field (field at which a luminance of 0.01 cd m^{-2} is detected) increases with the concentration. The maximum luminance we could obtain with the devices based on the 3.06% blends and above, is too small (less than 100 cd m^{-2}) for application in real devices. The emission of the LEDs changes from orange, for the MEH-PPV, to deep red upon increase of the porphyrin content. In terms of CIE coordinates,[13] they change from ($x = 0.59$, $y = 0.40$) for MEH-PPV to ($x = 0.68$, $y = 0.29$) for the 9% blend-containing LED. The EL CIE coordinates for the 0.34% ($x = 0.62$, $y = 0.36$) and 1.4% ($x = 0.66$, $y = 0.31$) blends are quite close to ideal red for full colour displays,[11] and these devices exhibit luminances of 220 cd m^{-2} and about 100 cd m^{-2}, respectively.

As shown in Fig. 4c, the increase of the porphyrin concentration brings about a marked decrease of the EL efficiency (expressed in cd A^{-1}). Note also that, in view of the specific response of the human eye, the red shift of the emission leads to a reduction of the luminance expressed as cd m^{-2}, in addition to the decrease of the EL quantum efficiency (photons per electron).

It is interesting to compare the properties of the blends reported here with those of copolymers of TPP-d and MEH-PPV. The effect of the porphyrin concentration on the electro-optical characteristics of the copolymer-based LEDs[11] is similar to that found for the blends: the current density, the luminance and the EL efficiency decrease with concentration, as found for single-layer devices.[11] We should mention, however, that comparing the characteristics of the devices based on the **CP2** and **CP3** copolymers, which have the highest porphyrin content (4.77% and 10.84% porphyrin by weight, respectively), we find that the LEDs based on **CP3** show usually similar or slightly higher current and luminance than those based on **CP2**. A lower turn-on field is also usually found for **CP3** based diodes.

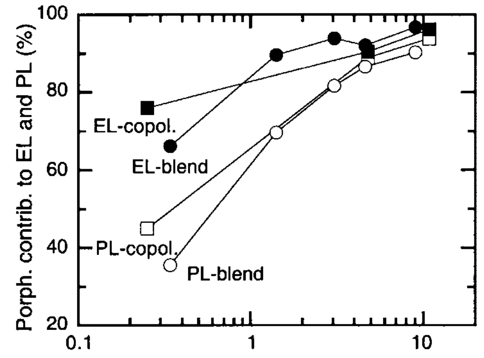

Fig. 3 Porphyrin contribution to the EL and PL emission spectra of both the blends and the copolymers. The porphyrin contribution has been estimated from the ratio of the area of its spectrum to the area of the overall spectrum.

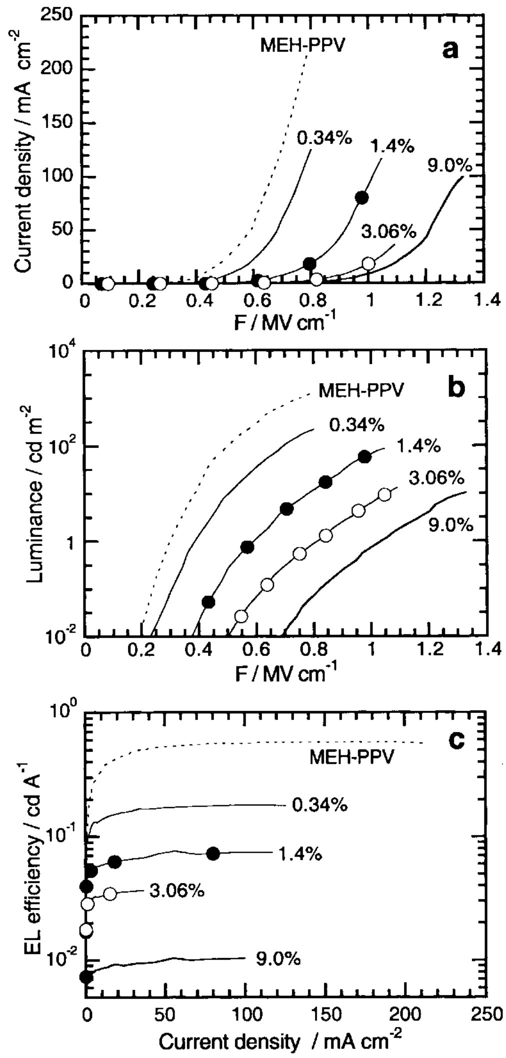

Fig. 4 Electro-optical characteristics of ITO/PEDOT/MEH-PPV : TPP-d blends/Ca LEDs: a) current density as a function of the applied electric field, b) Luminance as a function of the applied electric field; and c) electroluminescence efficiency as a function of the current density.

The energy transfer from MEH-PPV to the porphyrin is also evident in the EL spectra (for both the blends and the copolymers). The porphyrin contribution to the EL emission increases with the increase of the porphyrin concentration. We usually find a larger contribution of the porphyrin to the total emission in the case of EL compared to the PL spectra (see Fig. 3).

Table 1 compares the PL efficiency of the thin films on silica with the estimated internal quantum efficiency of the LEDs, for both the blends and the copolymers. Although the series is not complete, we find that the ratio between the PL and the EL efficiencies[14] is nearly constant for the blends with the lowest

Table 1 Relation between PL and maximum EL efficiencies (expressed as internal quantum efficiency) for the blends and copolymers. The LEDs structure is ITO/PEDOT/polymer/Ca

Porphyrin content of the blends (%)	η_{PL}/η_{EL}	Copolymers	Porphyrin content (%)	η_{PL}/η_{EL}
0	6.3	MEH-PPV	0	6.5
0.34	5.0	**CP1**	0.25	nd[a]
1.4	5.1			
3.06	7.0			
4.6	nd[a]	**CP2**	4.77	44.4
9.0	12.8	**CP3**	10.84	85.00

[a] Not determined.

porphyrin content, and similar to the ratio for neat MEH-PPV. For the samples with the highest porphyrin content this ratio increases, suggesting an increasing deviation from balanced concentrations of electrons and holes within the emissive layer.

It is interesting to note that the LEDs based on the 9.0% blend exhibit higher efficiency and luminance than those based on the copolymer **CP3**, with 10.84% porphyrin, suggesting that the hole–electron balance is worse in the case of the copolymer.

3. Discussion

As mentioned, the use of the specific host–guest pair (MEH-PPVand TPP-d) would suggest a low efficiency for the Förster transfer, in view of the small spectral overlap between the porphyrin absorption and the MEH-PPV emission (see Fig. 1). In fact, for the highest porphyrin content (9%), the MEH-PPV contribution to the total PL is only about 10% for excitation at 496 nm, although MEH-PPV absorption is predominant at this excitation wavelength.

The extent of the Förster transfer between a donor and an acceptor can be evaluated *via* the Förster radius, R_0, which identifies the distance at which transfer occurs with 50% probability. R_0 is given by eqn. (1)[15–17]

$$R_0 = \frac{0.5291 f^2}{n^4 N_A} \Omega \eta \mathrm{D} \tag{1}$$

where f^2 is an orientation factor (2/3 for randomly oriented molecules), n is the refractive index of the medium, N_A the Avogadro number and η_D is the PL efficiency of the donor. Ω is the spectral overlap integral, defined as in eqn. (2)

$$\Omega = \int_0^\infty \frac{\varepsilon_A(v) F_D(v)}{v^4} dv \tag{2}$$

where ε_A is the molar absorption coefficient spectrum of the acceptor, v the energy in wavenumbers and $F_D(v)$ the normalised emission spectrum ($\int F_D(v)dv = 1$).

From the normalised emission spectrum of MEH-PPV and the molar extinction coefficient spectrum of TPP-d, determined in a chloroform solution (1.22×10^{-5} M, ε (519 nm) = 9.92×10^3 l mol^{-1} cm^{-1}), we obtained $\Omega = 1.96 \times 10^{-14}$ l mol^{-1} cm^{-3}. Assuming $n = 1.7$, a value of $R_0 = 2.5$ nm results.[18]

This R_0 value compares well with the reported values of 4.8 nm for TPP dispersed in a blue-emitting ($\lambda_{max} \approx 441$ nm) polymer, PFO,[8] and of 3.3 nm for TPP in a green emitter ($\lambda_{max} \approx 500$ nm), Alq$_3$,[16] especially considering the relative overlap of the donor emission with the porphyrin absorption spectra and the much smaller value of the donor efficiency. We notice that the shorter R_0 and the poorer spectral overlap for the blends considered here are also reflected in the higher dopant concentration which is needed in order to achieve complete quenching of the host emission, approx. 9–10% here, as compared to approx. 1% in ref. 8.

The overall PL efficiency of the blends shows a monotonic decrease upon increase of the porphyrin concentration, indicating a quenching effect of the porphyrin, for which we identify two possible contributions: i) porphyrins aggregate at higher concentrations; ii) the porphyrins may favor exciton splitting, acting as quenching sites for the excitons in MEH-PPV, in addition to acting as exciton acceptors.

The "apparent" PL efficiency of the porphyrin in the blends (see Fig. 2b) increases on going from the 0.34% to the 1.4% blend. As mentioned above, this is the ratio of the photons emitted by the porphyrins divided by the number of total exciting photons, and not the the true efficiency of the porphyrin in that environment. This observation explains why this value is small at low concentration, although aggregation is expected to be low in that case, and the "true" PL efficiency is greater than the "apparent" value at higher concentrations. Note also that for the MEH-PPV blends we never get "apparent" PL efficiency values as high as those observed in the PVK blends (12.5%), which we attribute mainly to the low absorption of the porphyrin.

When we analyse these results in comparison with those of the copolymers we notice that the variation with porphyrin content is similar, although the overall PL efficiency of the blends is higher, probably as a result of the higher PL efficiency of the MEH-PPV used in the blends (about 19%) compared to that used in the preparation of the copolymers ($\approx 12.6\%$). Here we consider that the PL efficiency intrinsic to the MEH-PPV like backbone of the copolymers is similar to that of the neat MEH-PPV. This assumption appears to be supported by the fact that the difference between the overall PL efficiency of the blends and the copolymers is nearly constant up to porphyrin contents of 4.6% and 4.7%, respectively. This suggests there is no significant difference on the influence of the porphyrin on the PL efficiency when it is included as a dispersed chromophore or as a side group. However, as the distribution of the porphyrin chromophore within the polymer is not necessarily similar for the blends and copolymers, the differences in the efficiency of the energy transfer and in the concentration quenching effects, may also contribute. It is likely that the presence of the porphyrin as a side group may interfere with the polymerisation reaction, leading to differences in the luminescence properties intrinsic to the MEH-PPV like backbone. However, as evident in Fig. 3, the porphyrin contribution to the 0.34% blend is lower than for the 0.25% copolymer (**CP1**). The energy transfer appears thus to be more effective in the case of the copolymer. This difference is not significant for the samples with the two highest porphyrin contents, where the importance of the homogeneous distribution of the porphyrin becomes less important, in view of its higher concentration.

We also notice that the PL efficiency values of the blend and of the copolymer with the highest porphyrin concentration become similar, and we attribute this similarity to the dominant contribution of the porphyrin emission and the concentration quenching effects.

The electro-optical characteristics of the MEH-PPV based LEDs are strongly affected upon blending with the porphyrin. The current and the luminance decrease significantly upon increase of the porphyrin content (see Fig. 4). The luminance is, however, affected much more than the current, and so the EL efficiency decreases. Furthermore, the luminance turn-on field increases monotonically with the porphyrin content.

The results for the LEDs based on the copolymers, as a function of the porphyrin content, are similar.[11] However, at variance with the trend found for the blends and for the copolymers with lower porphyrin content, we have found that usually the LEDs based on **CP3** show similar or slightly higher current and luminance than those based on **CP2**. A lower turn-on field is also usually found. We have[11] tentatively attributed this behaviour to a transition from a detrimental porphyrin effect on the charge transport, for lower concentrations, to an active role, possibly associated to the surpassing of a percolation threshold for the transport mediated by the porphyrins.

The variation of the current and luminance turn-on field, common to both the blends and copolymer-based LEDs, is taken as an indication of a strong influence of the porphyrins on charge transport. Note, however, that the ratio between PL and EL efficiencies (shown in Table 1), only shows a strong increase for the blend with 9.0% porphyrin content.

Cyclic voltammetry (CV) studies on the copolymers[10] showed that the presence of the porphyrin results, on the reduction side, in the appearance of a small shoulder at lower potential than the reduction peak of MEH-PPV. From the existence of this shoulder, and considering that the reduction peak of MEH-PPV is not shifted upon inclusion of the porphyrin, we conclude that the electron affinity (EA) of porphyrin chromophores is slightly higher than the EA of MEH-PPV. Therefore, the porphyrins may act as electron trapping centers. Although no CV information could be obtained on the oxidation, we expect the ionisation potential (IP) of the porphyrins to be smaller than that of MEH-PPV, as the difference between the energy gap of the porphyrins and that of MEH-PPV is greater than the difference in EA. That is, the HOMO of the porphyrins is expected to lie at higher energy than the HOMO of MEH-PPV. Therefore, the porphyrin units may also act as hole trapping sites. In view of the strong decrease of the current and the strong increase of the luminance turn-on electric field (see Fig. 4b) it is likely that the holes are in fact more strongly trapped than the electrons.

We interpret the decrease in the current flowing through the devices, based either on the blends or on the copolymers, upon increase of the porphyrin content, as a result of two contributions: charge localisation at the porphyrin sites (slightly higher EA and presumably higher HOMO energy) and increase of structural disorder induced by the presence of the porphyrin.

The EL spectra show also evidence for the energy transfer as found in the PL. However, the porphyrin contribution to the total EL emission of the blends and of the copolymers is usually higher than to the PL, particularly for the samples with the lowest porphyrin content, as shown in Fig. 3. In the EL we expect triplets to be formed, but we do not expect these to beat the origin of the higher porphyrin emission in EL (as previously reported for platinum containing porphyrin),[2,4] as the free base TPP is reported to be non-phosphorescent,[6] and therefore, we do not expect the triplets to decay radiatively. A plausible explanation is the occurrence of charge trapping at the porphyrin sites, as mentioned above, leading to exciton formation and decay in these centers, besides the decay of the excitons transferred from the MEH-PPV. This would lead to an additional porphyrin contribution, compared to the PL.

We also note that, particularly for the blends with highest porphyrin content, the decrease in the EL efficiency is larger than the decrease in the PL efficiency, in comparison with MEH-PPV. We conclude that the yield of exciton formation (number of excitons formed per electron flowing in the external circuit) decreases at high porphyrin content. It is not clear at this point if this is due to a) an increasing charge imbalance within the emissive layer, as a result of an increased localisation of holes, and therefore less efficient electron injection, owing to less effective band-bending in proximity of the cathode, or b) a decrease in the bipolar recombination coefficient, that is proportional to the sum of electron and hole mobilities, in a Langevin-type recombination model.[19]

Finally, we should note that LEDs based on the two different batches of MEH-PPV exhibit slightly different characteristics, in agreement with the different PL efficiency. The differences found in the EL efficiency reflect the differences of the PL efficiency, which is higher for the MEH-PPV used in the blends. This is in agreement with similar values of the η_{PL}/η_{EL} ratio shown in Table 1, demonstrating that the differences in EL efficiency are the result of the differences in the efficiency of the radiative decay of the excitons, evaluated *via* η_{PL}.

4. Experimental

The preparation of the porphyrin chromophore and of the copolymers was previously reported.[10] The blends were prepared by mixing of the appropriate amounts of porphyrin and MEH-PPV in chloroform. MEH-PPV used here was prepared similarly to that used in the copolymers study (following the Gilch methodology). The amount of porphyrin ranges from 0.34% up to 9.0%, by weight. Three copolymers, identified as **CP1**, **CP2** and **CP3**, having porphyrin (TPP-d) contents of 0.25%, 4.77% and 10.84%, by weight, respectively, were characterised. These copolymers were identified in ref. 10 as **1c**, **1d** and **1e**, respectively. Optical absorption and PL studies were carried out on films deposited, by spin coating, on spectrosil B discs. The PL efficiency of the MEH-PPV:TPP-d blends was determined as reported by de Mello *et al.*,[20] using an integrating sphere, upon excitation at 496 nm. In the preparation of light-emitting diodes, LEDs, a layer (~40–45 nm thick) of PEDOT:PSS (BayerAG), cured under vacuum (200 °C for 4 h), was used to improve hole injection[21] into the emissive layer. The blend solutions were then deposited, by spin coating, on the ITO/PEDOT substrates, to give film thicknesses in the range 190–250 nm, as determined by a Dektak profilometer. Similar devices with MEH-PPV were about 102 nm thick. The diodes structure was completed by thermal evaporation of calcium, which was protected with an overlayer of aluminium, defining pixel areas of about 4 mm^2. The LEDs were tested under vacuum (at 10^{-2} mbar). The internal EL efficiency values were estimated according to Greenham *et al.*,[22] by multiplying the external EL efficiency values by $2n^2 = 4.5$, n being the refractive index. EL and PL spectra were obtained with a CCD UV-enhanced spectrograph (Oriel).

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