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# Efficient red- and orange-light-emitting diodes realized by excitation energy transfer from blue-light-emitting conjugated polymers

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The emission color of polymer-light-emitting diodes (PLED's) can be tuned by doping the active polymer layer with certain dyes or other fluorescent polymers. We demonstrate the realization of red-orange PLED's by *doping* a blue-light-emitting ladder-type poly(paraphenylene) ($m$-LPPP) with a new red-light-emitting polymer poly(perylene-co-diethynylbenzene) (PPDB). For PPDB concentrations far below 1 wt % the photo- (PL) and the electroluminescence (EL) spectrum of the $m$-LPPP/PPDB blend is already dominated by the PPDB emission because of an excitation energy transfer from $m$-LPPP to PPDB. The reason for this efficient energy transfer can be explained by the energetic position of the highest occupied and lowest unoccupied states in PPDB relative to the corresponding levels in $m$-LPPP. Besides the change in the emission color by doping PPDB into $m$-LPPP, a significant increase in the PL quantum efficiency (up to 41%) and even a more pronounced improvement of the external EL quantum efficiency of these PLED's (up to 1.6%) is observed. [S0163-1829(97)02928-7]

## INTRODUCTION

One very promising application of organic light-emitting diodes (LED's) is their usage in self-emissive flat panel color displays.[1–9] Several principles for the realization of the red-green-blue (RGB) color dots building up the multicolor displays have been suggested.[10–12] One of the most attractive methods, with respect to the ease of production, for fabricating RGB color dots is a color-conversion technique, which is based on efficient blue LED's covered with suitable dye layers[11,13,14] and dielectric filters and/or mirrors.[15] This organic color-conversion technique allows one to generate very efficient green light, by covering the blue EL emission with a green dye layer, which is excited by the blue EL emission and subsequently emits photoluminescence (PL) light in the green spectral range. Using this principle one can achieve blue-green quantum conversion efficiencies up to 90% resulting in a sixfold increased luminance value in the green compared to the blue emission.[16] However, the color conversion from the blue into the red is more difficult and also less efficient than the blue-green conversion, since the absorption of red dyes in the blue is usually very low, so that the maximal achievable luminance of the red light is significantly below the luminance of the blue EL pumping light.[15,16] One alternative way to this *external* color-conversion technique is to convert the blue emission *internally* into efficient red emission by blending the blue-light-emitting active layer with red dyes or red-light-emitting polymers.[17] This internal color-conversion technique based on blue LED's allows one to realize all visible emission colors. However, the accomplishment of red emission is of special interest, since the photoluminescence (PL) quantum efficiency of red light-emitting homopolymers and hence the achievable electroluminescence quantum efficiencies of red homopolymer LED's are comparably low.[18,19] The internal color-conversion technique is based on an internal excitation energy transfer from the host to the guest material, so that a down conversion of the emission color is achieved. In order to realize efficient and stable LED's with this technique, guest materials with a high PL quantum efficiency and/or good charge transport properties are requested.[20–24]

We present EL devices based on a blend of blue-light-emitting methyl substituted ladder-type poly(paraphenylene) ($m$-LPPP) and a new red-light-emitting poly(perylene-co-diethynylbenzene) (PPDB). For a concentration of around 1 wt % of PPDB in the LPPP/PPDB blend, an almost complete excitation energy transfer from $m$-LPPP to PPDB occurs and the emission of the polymer blend consequently is dominated by the red-orange PPDB emission. The maximum EL quantum efficiency is observed, using active layers containing only 0.2% wt % of PPDB in $m$-LPPP. In single-layer EL devices these maximum values correspond to external EL quantum efficiencies of 1.6%. When the energy transfer from the blue to the red is partly hindered by a charge-carrier blocking material, efficient white LED's based on this polymer blend can be obtained.[25]

## EXPERIMENT

The polymers investigated in this work are $m$-LPPP and PPDB, the synthesis is described in Refs. 26 and 27 (Fig. 1). The EL devices were built in a simple single-layer configuration using indium-tin-oxide (ITO) and Al as air stable electrodes. The active polymer layers of the EL devices were produced by spincoating.

The measurement of the absolute PL quantum efficiency was performed in an integrating sphere based on a method described in Ref. 28. The EL spectra were recorded with a CCD spectrometer 77400 LOT-ORIEL. The ionization potential of the polymers was determined by cyclic voltamme-

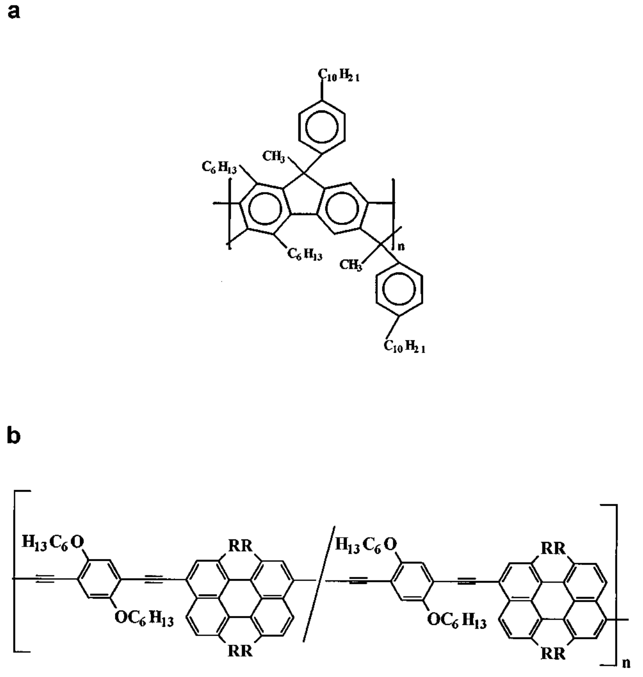

FIG. 1. Chemical structure of (a) LPPP and (b) PPDB ($R$ = phenoxy-$t$-butyl).

try measurements with a method described in Ref. 29.

## RESULTS AND DISCUSSION

The optical and electronic properties of the conjugated polymer $m$-LPPP, which has the most uniform conjugation length and the best environmental stability of all LPPP's presently available, are already thoroughly investigated.[30–33] The absorption spectrum of $m$-LPPP is characterized by a steep onset at 2.69 eV and by well-resolved vibrational split maxima (Fig. 2). The PL spectrum is homologous to the absorption spectrum and the dominant PL maximum is only very slightly Stokes shifted ($\approx 0.04$ eV). The high intrachain order of $m$-LPPP is reflected in a high PL quantum efficiency $\eta_F$ up to 100% in solution and around 30% in films.[32] This comparably high solid-state $\eta_F$ is further increased by doping the new red-light-emitting polymer PPDB into $m$-LPPP (Figs. 1 and 2). For very small PPDB concentrations the absolute PL efficiency rapidly increases up to 41% (for PPDB concentrations of 0.7 wt % in the blend). For higher doping concentrations $\eta_F$ then slowly decreases (down to 11% for 10 wt % PPDB in the blend) and approaches the $\eta_F$ value of pure PPDB films, which is only 0.6%. The PL spectra of the $m$-LPPP/PPDB blends were recorded at an excitation wavelength of 420 nm, where mainly $m$-LPPP is excited because the absorption of $m$-LPPP at this wavelength is much stronger than that of PPDB (Figs. 2 and 4). The PL spectra of this blend, in which the concentration of $m$-LPPP is much higher than that of PPDB, however, are dominated by the red-orange PPDB emission due to an efficient energy transfer from $m$-LPPP to PPDB (Fig. 4). Even at doping concentrations of 0.2 wt % PPDB in the blend the maximum of the red emission, which stems from PPDB, is already twice as high as the $m$-LPPP emission, so that the emission color of this blending concentration looks orange [CIE (Ref. 34) coordinates $x = 0.46$, $y = 0.4$]. For doping concentrations above 3.5% PPDB the $m$-LPPP emission component in the PL spectrum has nearly vanished and the red PPDB emission remains.

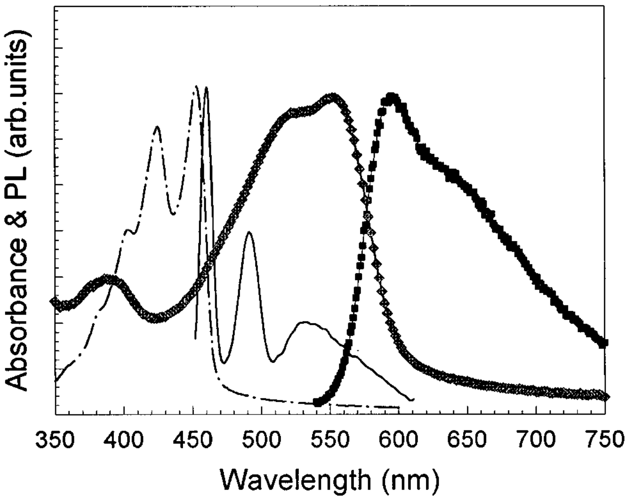

FIG. 2. Absorption of $m$-LPPP (--), photoluminescence of $m$-LPPP (—), absorption of PPDB (♦), and photoluminescence of PPDB (■).

In order to understand the mechanisms in the polymer blend we first have to discuss the optical and electronic properties of the PPDB polymer. The absorption and PL spectrum of a PPDB film are depicted in Fig. 2. In the absorption spectrum the dominant peak resulting from the $\pi$-$\pi^*$ transition occurs at 554 nm and its vibrationally split shoulder is located at 525 nm. At around 390 nm an additional absorption peak is observed; which is attributed to an electronic excitation of the perylene group on the backbone of the PPDB. The shape of the PL spectrum is homologous to the absorption spectrum. The dominant emission maximum, which is located at 595 nm, is 0.16 eV Stokes shifted compared to the dominant absorption peak. The red PPDB emission color can be quantified in CIE coordinates $x = 0.61$ and $y = 0.39$. The absolute PL quantum efficiency of the PPDB in the solid state is very low ($\approx 0.6\%$). This low $\eta_F$ value is mainly due to interchain quenching effects, because $\eta_F$ drastically increases, when the polymer chains are isolated from each other as is the case in liquid or solid solutions. In diluted liquid solutions values for $\eta_F$ above 60% and in solid solutions [3 wt % PPDB in poly(methylmethacrylat)] efficiencies of 20% are observed. The interchain interaction in the solids results in a formation of weaker bound interchain excited states. The radiative recombination of these interchain excited states is less efficient compared to the emission of the intrachain excitons and is responsible for the development of a long-wavelength tail in the solid-state PL spectrum, which is less significant in the PL spectrum of diluted liquid or solid solutions (Figs. 2 and 4).

In the $m$-LPPP/PPDB films no phase separation can be detected within the resolution ($>10$ nm) of an atomic force microscope. The efficient excitation energy transfer in the $m$-LPPP/PPDB blends can therefore be understood, when we compare the energetic levels of the two polymers. The ionization potential and the lowest excited states of PPDB are located inside the energy gap of $m$-LPPP (Fig. 3). An effec-

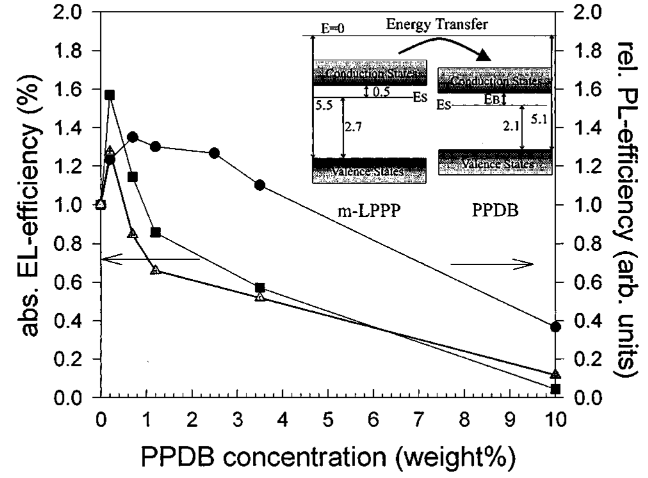

FIG. 3. Absolute electroluminescence quantum yield $\eta_{\mathrm{EL}}$ (■), relative photoluminescence quantum yield $\eta_F$ (●), and the efficiency of singlet exciton formation $\eta_R$ (▲) [obtained from Eq. (1) using the experimental data for $\eta_{\mathrm{EL}}$ and $\eta_F$, under the assumption that $\gamma=\mathrm{const}$] of the $m$-LPPP/PPDB blend depending on the PPDB concentration (in wt %) in the blend. Inset: scheme of the energetic levels of $m$-LPPP and PPDB. The values for the highest occupied states were deduced from cyclic voltammetry (Ref. 29). The position of the excitonic levels was obtained by adding the energy gap to the ionization potential. The difference between exciton states ($E_S$) and the lower edge of the unoccupied states corresponds to the exciton binding energy $E_B \approx 0.5$ eV for $m$-LPPP (Ref. 38).

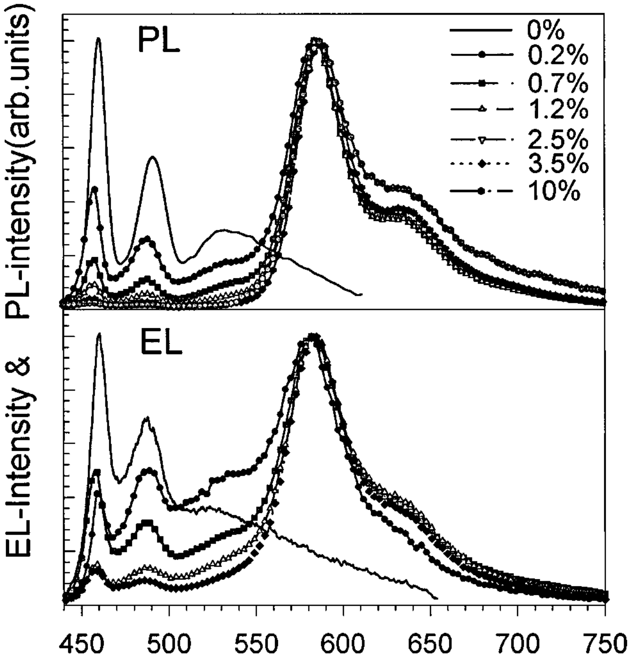

FIG. 4. Electroluminescence (EL) (recorded from ITO/$m$-LPPP:PPDB/Al devices with a bias voltage of 15 V, $d_{\mathrm{polymer}} \approx 85$ nm) and photoluminescence (PL) ($\lambda_{\mathrm{excitation}}=420$ nm) spectra of the $m$-LPPP/PPDB blend depending on the PPDB concentration in the blend.

tive excitation energy transfer therefore occurs from $m$-LPPP to PPDB. In a particle picture this excitation energy transfer can be described as a transfer of electrons (negatively charged polarons), holes (positively charged polarons), or entire excitons from $m$-LPPP into energetically preferably PPDB states. The charge carriers, which are transfered to PPDB, are subsequently confined to PPDB, as PPDB together with surrounding $m$-LPPP forms a ''quantum well'' for the charge carriers. The $e$-$h$ pairs, which are created in $m$-LPPP by photoexcitation, therefore migrate to the PPDB polymer chains, where they recombine with a high probability, so that the PL efficiency is higher compared to pure $m$-LPPP films (Fig. 3). The upper limit of the PL quantum efficiency in the $m$-LPPP/PPDB polymer blend is given by the PL quantum yield in PPDB solution ($\approx 60\%$). For PPDB concentrations above 0.7% in the blend $\eta_F$ decreases, due to the fact that PPDB interchain quenching processes are becoming dominant (Fig. 3).

$m$-LPPP is a very suitable material as a blue-light-emitting layer in EL devices due to its high PL quantum efficiency, good charge transport properties, and high environmental stability.[32] The values for the external EL efficiency of the best devices in an ITO/$m$-LPPP/Al configuration are currently around 1% due to a recent improvement in the preparation condition compared to cw operation values of around 0.1%, which were reported earlier.[32] By using active layers of $m$-LPPP doped with a small amount of PPDB the blue EL emission can be converted into orange and red EL emission and the considerable high EL efficiency of the $m$-LPPP devices can be significantly increased. The maximum external EL efficiency of 1.6% is obtained at very low doping concentrations of only 0.2 wt % PPDB in $m$-LPPP (Fig. 3). This value of the absolute EL efficiency is superior or at least comparable to that reported for red and orange homopolymer LED's in comparable configurations up to now.[19] The increased EL efficiency can be explained by the good confinement of $e$-$h$ pairs at PPDB sites, where they have a high probability for radiative recombination, as will be pointed out below.

For PPDB concentrations above 0.2% in the $m$-LPPP matrix the EL efficiency first rapidly decreases and then slowly approaches the value for pure ITO/PPDB/Al devices, which is only 0.01%. A qualitatively similar dependence of the EL efficiency on the guest-host concentration was observed for other doped organic metal complexes and other semiconducting polymer blends.[20,35]

The shape of the EL spectra of the polymer blend is very similar to the PL spectra, reflecting the efficient energy transfer from the $m$-LPPP into the PPDB (Fig. 4). For doping concentrations of only 0.2 wt % PPDB in $m$-LPPP the spectrum is already dominated by the red component and for PPDB concentrations higher than 3.5% the blue part in the spectrum has nearly vanished. The energy transfer can be controlled, when a hole-blocking material is inserted into the polymer blend.[36] In this case the color can be controlled with the magnitude and the polarity of the applied bias voltage and it is also possible to produce efficient white LED's.[25]

The dependence of the EL efficiency on the PPDB concentration is similar to the concentration dependence of the PL efficiency. However, the EL efficiency reaches its maximum at lower doping concentration (0.2 wt % PPDB in $m$-LPPP) and decreases more rapidly for increasing doping concentration than the PL efficiency (Fig. 3).

In organic LED's the EL quantum efficiency $\eta_{\mathrm{EL}}$ has been described using following equation:[37]

$$\eta_{\mathrm{EL}} = \gamma \eta_R \eta_F , \qquad (1)$$

where $\gamma$ is a double-charge injection factor, $\eta_R$ is the efficiency of singlet exciton formation, and $\eta_F$ is the quantum efficiency of fluorescence.

The EL and PL efficiencies depend in a different way on the PPDB concentration in the $m$-LPPP matrix (Fig. 3), so that at least one of the two other parameters in Eq. (1), besides $\eta_F$, strongly depends on the PPDB concentration in the blend. The charge-carrier injection and implicitly $\gamma$ are only slightly influenced by doping $m$-LPPP with PPDB (for PPDB concentrations up to 3.5%), as the threshold electric field and the slope of the current and of the EL intensity of these EL devices is not significantly different compared to homopolymer $m$-LPPP devices.

In contrast, the third factor in Eq. (1), the efficiency of singlet exciton formation $\eta_R$, is strongly altered by the amount of PPDB (Fig. 3). For low concentrations of PPDB in the polymer blend the charge transport in the EL device is mainly provided by $m$-LPPP. PPDB acts as an effective trap for electrons and holes in the blend and therefore enhances the singlet exciton formation $\eta_R$ and also the EL quantum efficiency (Fig. 3). When the concentration of PPDB further increases, the trapping of the charge carriers is a drawback to achieve efficient EL because in the EL device the charge carriers are injected from opposite sides of the device and then have to drift through the device in order to meet each other, interact, and form the emitting species. In $m$-LPPP/PPDB blends containing a high PPDB concentration many charge carriers are trapped by PPDB near the electrodes, where they have been injected. Especially holes, which are captured near the anode, have only a low probability to interact with electrons (as the recombination zone for $m$-LPPP devices is located near the cathode[33]) and therefore the exciton formation yield $\eta_R$ in the blend decreases. Additionally the efficiency for radiative recombination $\eta_F$ of the created emitting species decreases for higher PPDB concentrations, so that according to Eq. (1) the EL efficiency is strongly reduced for high PPDB concentrations in the blend (Fig. 3).

## CONCLUSION

We discussed the optical properties of a polymer blend consisting of the blue-light-emitting polymer $m$-LPPP, which is slightly doped with a new red-light-emitting polymer PPDB and we presented the application of this polymer blend in LED’s. The optical properties of the $m$-LPPP/PPBD polymer blend are characterized by a very effective excitation energy transfer from $m$-LPPP into the states of PPDB. In the quantum well-like structure of the $m$-LPPP/PPDB polymer blend a maximum PL efficiency of 41% for only 0.7 wt % PPDB in $m$-LPPP is obtained. In LED’s, using the $m$-LPPP/PPDB blend as the active layer, highly efficient EL emission with external quantum efficiencies up to 1.6% is obtained. The presented internal color-conversion technique will be applied to realize efficient polymer LED’s of user-defined emission color.

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