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Electric-field-induced luminescence quenching in an electroluminescent organic semiconductor

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We report on the effect of a static electric field on the photoluminescence (PL) of laddertype poly(paraphenylene) (*m*-LPPP) in devices of polymer-light-emitting diodes. External electric fields of 4.5 MV/cm reduce the integral PL intensity down to 24% of the zero-field value and alter the shape of the PL spectra. The field-induced PL quenching in the *m*-LPPP polymer is ascribed to field dissociation of the emitting species. Time-resolved spectroscopy showed that the emission is composed of contributions from the radiative recombination of free singlet excitons and of a second emitting species, which we describe as self-trapped excitons. The observed field-induced changes of the shape of the PL emission can be attributed to the different field response of these two emitting species. Thus the PL emission color can be changed with the electric field in the blue-green spectral range. The magnitude of the binding energy of free singulet excitons is discussed. [S0163-1829(97)11907-5]

I. INTRODUCTION

After the application of conjugated polymers as organic semiconductors in light-emitting devices was demonstrated,[1,2] poly(paraphenylene) (PPP) was the first simple conjugated polymer to produce visible blue light emission when used as an active layer.[3] Although PPP obtained from precursor routes shows appreciable disorder and high impurity concentrations, remarkably high EL efficiencies up to 0.05% were achieved.[3] A substantial improvement of the performance of the polymer in electroluminescence (EL) devices was expected by tying the PPP backbone into a planar, rigid ribbon structure (see e.g., Fig. 1), so that a defined conformation is obtained. The ladder-type PPP (LPPP) (for details of synthesis, see Ref. 4), is a soluble and easily processable polymer showing a photoluminescence (PL) quantum efficiency higher than 70% in solution.[5] The optical and electronic properties of the LPPP are already well characterized.[6–10] The LPPP polymer was also successfully used in EL devices but an improvement of the EL efficiency and lifetime compared to PPP, which was expected especially due to the high intrachain order, was not obtained.[11,12] The EL and the PL spectra of the LPPP are dominated by a yellowish component due to the presence of aggregates in the ground state or in the excited state (excimers).[5,10] The creation of the aggregates is enhanced by temperature[13] and to a lesser extent by degradation processes of the polymer. The degradation of the LPPP is the limiting factor for the cw-operation lifetimes of EL devices based on LPPP and mainly occurs via a photo-oxidation of the hydrogen atom (at substitutent's position *Y*, see Fig. 1) induced by the combination of oxygen and UV light.

To improve the environmental stability, a LPPP polymer was synthesized with a methylene group at the position of the substitutent *Y*. This so-called *m*-LPPP has the highest and most uniform effective conjugation length in the family of the LPPP's up to now and exhibits—as a consequence of its high intrachain order—a PL quantum efficiency with values up to 100% in solutions and higher than 30% in thin *m*-LPPP films.[14] The EL devices produced with *m*-LPPP as the active layer show high EL quantum efficiencies (up to 4%) and comparably high cw operation lifetimes in air up to 170 h.[14] It has been observed that the EL efficiency of the *m*-LPPP polymer-light-emitting diodes (PLED's) saturates or even decreases, when the devices are operated with electric fields high above the threshold field. A better understanding of the radiatively relaxing species and the mechanisms of quenching in the device is therefore crucial for optimizing the overall quantum efficiency of the PLED's. The electric-field-induced quenching of the emitting species of the EL corresponds to that of the PL. This fact is not surprising since it is assumed that the EL and PL originate from the same excited species.[1] The *m*-LPPP is also a promising material for optically and also electrically pumped solid-state polymer lasers, because stimulated emission does not compete with dissipative processes in the polymer (like photoinduced absorption).[15] For the application of the

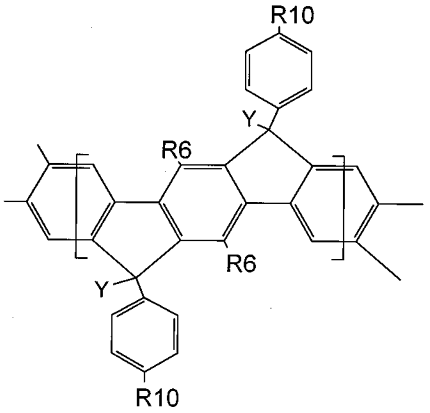

FIG. 1. Chemical structure of *m*-LPPP: R_6:-C_6H_{13}; R_{10}:-$C_{10}H_{21}$; Y:-CH_3.

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m-LPPP in polymer lasers, it is also important to know by which means the high local electric fields influence the radiative recombination of the emitting species.

The field dependence of the PL was extensively investigated for another conjugated polymer—a soluble poly(phenylphenylene-vinylene)—in polystyrene blends (PPV/PS) by Bässler *et al.*[16–19] Femtosecond time-resolved PL measurements revealed that the field-induced luminescence quenching is not an instantaneous process.[16] This shows that the formation of singlet excitons is hardly effected by the field, whereas their radiative decay strongly depends on the external field. Thus the magnitude of absorption in the range of the excitation energy of the singlet excitons only slightly changes with the applied electric field.[20] In contrast, the lifetime of the singlet excitons is drastically reduced by the electric field, i.e., by opening nonradiative decay pathways within the first picoseconds after excitation resulting in a strong quenching under electric fields.[19]

We report on the dependence of the steady state PL of the *m*-LPPP homopolymer on static electric fields. A maximum PL quenching of 76% is obtained for a magnitude of the applied field of 4.5 MV/cm. When the electric field exceeds a magnitude of 2 MV/cm the dominant peak in the PL spectrum, located at 461 nm, is less efficiently quenched than the two other peaks at 491 nm and 530 nm. Therefore the colour of the PL emission can be controlled by the external field in the blue-green spectral range.

II. EXPERIMENT

The *m*-LPPP (the polymer synthesis is described elsewhere[21,22]) was dissolved in oxygen-free toluene by stirring at 60 °C for several hours under inert conditions. The EL devices were produced by spin coating the *m*-LPPP solution onto indium-tin-oxide (ITO) -coated glass substrates (Baltracon Z20) in an argon glove box. The ITO, which was thoroughly cleaned and heat treated before, is used as the transparent conducting bottom electrode. After the *m*-LPPP layer has been annealed in high vacuum at 80 °C for several days, high-purity Al was evaporated (below 10^{-6} mbar) for the top electrode onto the polymer. The thickness of the *m*-LPPP layer was determined via Tolansky's interferometric method and absorption measurements (with a Perkin Elmer λ9 spectrophotometer). The PL spectra were recorded with high-resolution equipment (Jobin Yvon HR640 monochromator, cooled Hamamatsu photomultiplier R943-02). The samples were excited with a 1000-W Xe lamp in combination with a Jobin Yvon double monochromator H10 D UV. To obtain the field-dependent PL spectra, the excitation (≈ 60 μW/cm^2) and detection were performed through the ITO side of a free standing device (ITO/*m*-LPPP/Al) in air at room temperature. The leakage current, which passes through the device due to the high applied electric fields, causes Joule heating of the sample during the experiment. To determine the field-induced change of the PL spectrum and avoiding temperature effects—relatively short bias pulses ($t=0.5$ s) and long pauses ($t=15$ s) between each step of the scan for the PL measurement were introduced.

The temporal decay and the spectral evolution of the PL have been studied by picosecond spectroscopy. The excitation pulses were provided by a Ti:sapphire laser setup and the detection was accomplished by a streak camera (Hamamatsu synchroscan) in combination with a spectrometer.

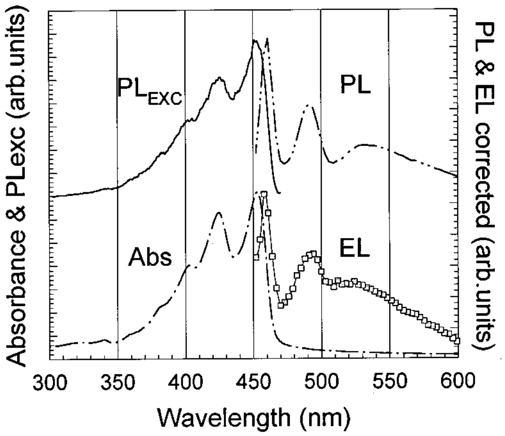

FIG. 2. Absorbance spectrum (dashed-dotted line), PL excitation spectrum (solid line) (emission at 491 nm), PL emission spectrum (dashed-dot-dotted line) (excitation at 420 nm) and EL spectrum (squares) (ITO/*m*-LPPP/Al) of a *m*-LPPP layer ($d \approx 90$ nm) (PL and EL are corrected for self-absorption).

III. RESULTS AND DISCUSSION

The absorption and the excitation spectra of the conjugated polymer *m*-LPPP are characterized by a steep onset at 2.69 eV due to a π-π^* transition and by well-resolved maxima (see Fig. 2). The PL and also the EL spectra are homologous to the absorption spectrum and their dominant maximum is very slightly Stokes shifted to the absorption maximum. Due to the strong overlap between absorption and PL spectra, the relative intensity and the location of the dominant PL and EL peak ($\lambda=461$ nm) is strongly influenced by self-absorption effects. The self-absorption was taken into account via a correction of the PL spectrum considering the geometry of the experiment and the optical density of the sample. After applying this correction a value for the Stokes shift of 0.036 eV is obtained, which is in the same order of magnitude as the thermal energy kT at room temperature.

To investigate the electric-field effect on the PL intensity, the PL was recorded from a device (ITO/*m*-LPPP/Al) on which a bias voltage was applied. In the *forward* direction (ITO as anode) the onset of the current and also the EL emission occurs, when the electric field exceeds a threshold field [usually between 0.5 and 1.5 MV/cm (Ref. 14)]. In order to avoid that EL emission overlaps the PL emission, the PL measurements were performed by applying *reverse* bias voltages or small forward bias voltages (<0.5 MV/cm). Moreover, it was always verified that no EL emission was detectable, before the field-dependent PL measurements were performed. The *m*-LPPP polymer layer is not charge depleted by applying reverse fields up to 3 MV/cm (in contrast to the case when forward electric fields are applied[23,24]). Therefore space charge regions, which would drastically affect the internal electric fields, do not have to be taken into account. The internal electric field slightly deviates from the external field due to a built-in electric field, which results from the difference of the work functions of the electrodes.

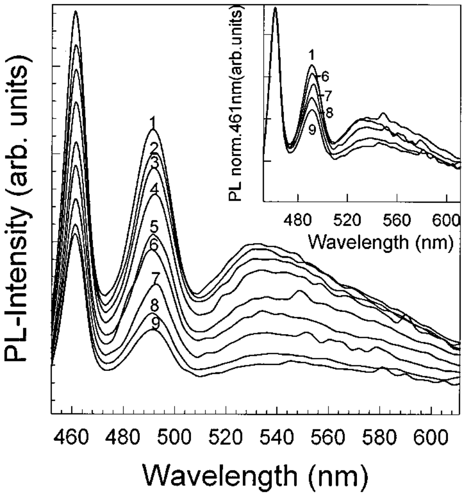

FIG. 3. PL (excited at 420 nm) depending on the applied field of a m-LPPP layer ($d \approx 90$ nm) at room temperature (*curve 1,* 0 MV/cm; *curve 2,* 1.5 MV/cm; *curve 3,* 1.8 MV/cm; *curve 4,* 2.0 MV/cm; *curve 5,* 2.2 MV/cm; *curve 6,* 2.4 MV/cm; *curve 7,* 2.9 MV/cm; *curve 8,* 3.3 MV/cm, *curve 9,* 4.4 MV/cm) (inset: spectra normalized to the intensity of the peak at 461 nm).

For the ITO/m-LPPP/Al device configurations the built-in voltage is determined to be around 0.7 V, which corresponds to a built-in field of 0.07 MV/cm for an active layer with a thickness of 100 nm.

The dependence of the PL spectrum on the applied reverse external electric field E is shown in Fig. 3. The PL intensity (I_{PL}) and hence the PL quantum efficiency strongly decrease for an increasing applied field, whereas the location of the PL peaks remains unchanged. The relative change of the PL intensity associated with the applied electric field is spectrally dependent. The PL quenching (Q_{PL}), which is defined as

$$Q_{\mathrm{PL}}(E)=\frac{I_{\mathrm{PL}}(0)-I_{\mathrm{PL}}(E)}{I_{PL}(0)} \tag{1}$$

(where $I_{\mathrm{PL}}(0)$ is the intensity of the zero-field PL), of the integrated PL and of the PL peak components as a function of the external electric field E is shown in Fig. 4. The decay of the PL can be divided into three sections: the PL intensity slowly decreases for increasing external electric fields up to around 1.5 MV/cm, then the integrated PL emission decreases rapidly down to 33% (of its zero-field value), when the fields are increased up to 3.1 MV/cm. When the applied field is further increased, the quenching of the PL starts to saturate (24% at 4.45 MV/cm)—as it was also observed for inorganic semiconductors.[25]

The intensity of the peak at 461 nm is less efficiently quenched than the intensity of the other peaks in the spectrum. A correlation between the excitation wavelength (380–440 nm) and the field dependent PL has not been observed.

Several mechanisms associated with the application of an electric field may contribute to the PL quenching (*field-induced quenching*) in the device: (i) the leakage current (polarons) (see Fig. 5) can act as effective quenching sites for singlet excitons.[26] (ii) The applied voltage and the leakage current cause electrical power dissipation in the sample.

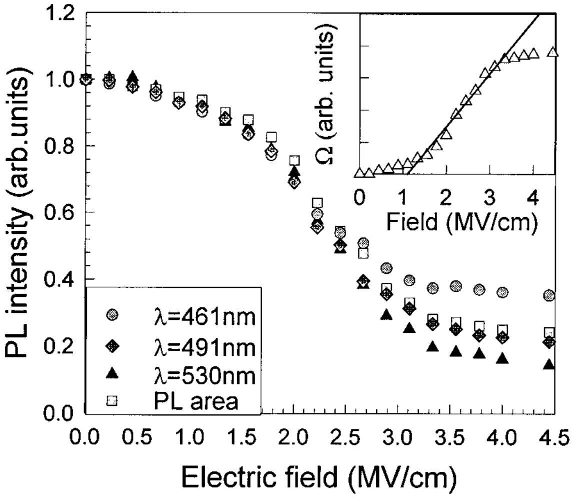

FIG. 4. Integrated PL, intensity of the peak at 461 nm, 491 nm, and 530 nm as a function of the external electric field [inset: the dissociation efficiency of the excitons Ω (triangles), which is derived from Eq. (2) using the experimental data of the PL intensity in dependence of the applied field. The solid-line models the slope of the transition region between 1.1 and 3.0 MV/cm. The intersection between the solid line and the x axis marks the onset for the PL quenching.]

The sample temperature therefore increases and thermal quenching is enhanced by collisional quenching mechanisms or by opening nonradiative decay paths for the excited species.[27] (iii) The kinetics of the emitting species are changed, so that they might be swept to the electrodes by the applied field.[28] The probability for nonradiative recombination of the emitting species at quenching sites, which are preferentially located near the electrodes, is therefore enhanced. (iv) The quenching due to a field-induced annihilation of the emitting species.

Current induced quenching was assumed to be responsible for PL quenching effects observed in organic field-effect transistor (FET) devices.[29,30] However, in this case it is not possible to explain the PL quenching solely with current induced quenching mechanisms as the magnitude of the PL quenching, we obtained at low leakage currents of around 10

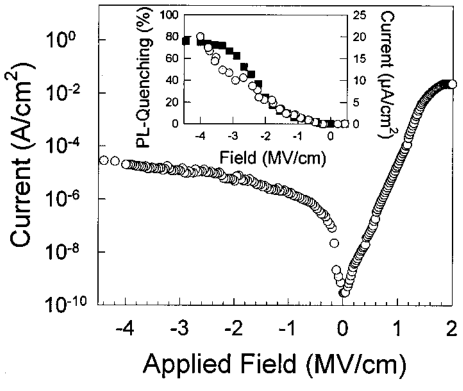

FIG. 5. Dark current vs electric field characteristics of the ITO/m-LPPP/Al [inset: PL-quenching (squares) and the current depending on the applied electric field (circles)].

μA/cm^2, is much higher than the PL quenching observed in FET devices, which was around 5%. Particularly the plateau at low applied fields ($<$1.2 MV/cm), and the saturation of the PL quenching at high fields ($>$3.5 MV/cm), cannot be satisfactorily described with current-induced quenching, as the quenching should follow the charge density in the sample but the quenching/field dependence does not coincide with the current/field characteristic (see Fig. 5). Furthermore, recent results show that the PL quenching for forward electric fields above 1 MV/cm is even lower than the PL quenching for reverse fields of the same magnitude, although the current in forward direction is several magnitudes of order higher than in the reverse direction.

The emitting species in the m-LPPP polymer are neutral, so that they are not supposed to move under the applied electric field. A field-induced sweeping of the emitting species towards the electrodes, which would increase quenching effects, is therefore very unprobable. The effect of temperature quenching on the shape of the PL is rather contrary to what we observe in Fig. 3 as it will be described later in more detail.

Therefore we propose that the field-induced annihilation of the emitting species is the most dominant process for quenching, which also allows to explain the spectrally nonuniform PL quenching, which is observed above a magnitude of 2 MV/cm of the applied electric field (see Figs. 3 and 4). The intensity of the dominant PL peak at 461 nm (and the area under the peak) decreases less pronounced than the intensity of the peak at 491 nm and the broad emission peak at approximately 530 nm. To interpret this phenomenon by field-induced annihilation, we will discuss the evolution of the PL emission process in the m-LPPP polymer. The time-resolved PL spectroscopy is a powerful method for studying the nature and dynamics of emission processes. Streak camera measurements on the m-LPPP polymer (for details see Ref. 31) reveal that two excited species with different lifetimes contribute to the PL emission (a behavior which is also observed in Ref. 15). The fast component ($\tau \approx 25$ ps) is attributed to the radiative decay of quasifree intrachain singlet excitons (SE). The emission peaks located at 461, 491, and 530 nm result from this spontaneous emission into the vibronic sidebands of the SE states.[32] The long living component ($\tau \approx 800$ ps) can be discussed in terms of the radiative recombination of self-trapped excitons (STE's),[33] leading to a rather broad emission peak centred at approximately 545 nm. In the time-integrated PL, the broad emission masks the vibronic peak at 530 nm, while it contributes as an intensive background to the peak at 491 nm and negligible to the dominant peak at 461 nm (see Fig. 2).

When electric fields are applied usually competitive processes to the radiative decay of the excitons, as their field induced dissociation occur. The Onsager theory is often used to describe the field-dependent decay of the PL intensity (I_{PL}) due to charge separation:

$$I_{\mathrm{PL}}(E) = \frac{k_r}{k_r - k_n}\,[I - \eta_{\mathrm{PL}}\Omega(E)]I_{\mathrm{ex}}, \tag{2}$$

where k_r and k_n are the rate constant for radiative and nonradiative decay, η_{PL} is the PL quantum efficiency, $\Omega(E)$ is the probability for the dissociation of electron-hole pairs into free charge carriers depending on the applied electric field, and I_{ex} is the building rate of the excitons. Except the dissociation efficiency Ω, all parameters in Eq. (2) are field independent. This also includes the nonradiative decay rate k_n, which only is field dependent in nonpolar organic materials for electric field strength above 10^7 V/cm.[34] The qualitative field dependence of Ω, derived from Eq. (3) using the experimental data of the field-dependent decay of the PL intensity of the m-LPPP, is depicted in Fig. 4. In organic photoconductors often a slightly different dependence of I_{PL} on the electric field is observed which is attributed to a dissociation of the excitons into bound electron-hole pairs, which may subsequently return to the primary excited state or be dissociated into free carriers from this states.[26] In semiconductors the Poole-Frenkel effect, which describes the field-assisted thermal dissociation of excitons, is often successfully applied to describe the observed PL quenching.

In the case of m-LPPP the PL quenching can be well described using the Onsager model for field induced dissociation of SE external electric fields up to 2 MV/cm. For electric fields above 2 MV/cm the stronger bound STE are also dissociated, therefore the PL intensity resulting from the spontaneous decay of the SE decreases less pronounced than the broad emission peak, which stems from the radiative decay of the STE at approximately 530 nm (see Figs. 3 and 4). The nature of the plateau of the PL quenching at high electric fields is not fully understood but might be explained by deviations of the internal electric field from the external field due to the developing of space charge zones at such high applied electric fields.

A crude estimation of magnitude of the excitonic binding energy in the m-LPPP can be obtained from the observed PL quenching by assuming the following scenario.

The electric potential changes the Coulomb potential in which the excitons are confined. The effective potential consists of a superposition of the Coulomb potential with the electric potential. In the asymmetric effective potential a maximum comes into existence which is lowered by ΔW:

$$\Delta W = 2e\sqrt{\frac{eE}{\varepsilon\varepsilon_0}} \tag{3}$$

(where ε is the dielectric constant) compared to the free ionization energy. By applying an external electrical field E the excitons will effectively dissociate when ΔW is approximately equal to the binding energy of the exciton E_B. When we take a value for the electric field of 1 MV/cm, which is obtained by subtracting the value for the built-in electric field from the value of the electric field at the onset of effectively PL quenching (see inset, Fig. 4), and use the anisotropic intrachain dielectric constant of the m-LPPP polymer [$\varepsilon_{\mathrm{LPPP}} \approx \varepsilon_{\mathrm{PPP}} = 10$ (Ref. 35)], Eq. (3) yields a value of around 0.8 eV for E_B. In this simple model some effects contributing to the observed PL quenching (as tunneling, temperature, or trapping of the dissociated excitons) were neglected, therefore this value gives an upper limit for E_B of free excitons. From electroabsorption measurements we obtain a value of $E_B \approx 0.5$ eV.[20]

As the m-LPPP polymer is a low-dimensional system, some aspects, as an additionally quantized exciton energy (due to an increased overlap between the electron and the hole building up the exciton), have to be taken into consideration.

The sample temperature also influences the shape of the PL spectrum. In case of temperature quenching the short-wavelength part is more effectively quenched than the long-wavelength part (just opposite to the electric field quenching). This change in the shape of the PL spectrum is accompanied by a decrease of the integral PL intensity due to overall thermal quenching.

IV. CONCLUSION

We studied the electric field-induced quenching of the PL intensity of the *m*-LPPP polymer in the configuration of PLED's. The decay of the PL can be divided into three sections: up to electric fields of around 1.5 MV/cm the PL intensity decreases slowly down to 82% of the zero-field value of the integrated PL emission. For electric fields up to 3.1 MV/cm the PL emission decreases rapidly down to 33% and tends to saturate for high applied fields (24% at 4.45 MV/cm). The field-dependent PL quenching is attributed to a field annihilation of the emitting species in the *m*-LPPP polymer. The field induced change of the shape of the PL and hence of the emission colour above 2 MV/cm, is attributed to the different field dependence of free singlet excitons compared to the self-trapped excitons, both representing the emitting species in the *m*-LPPP. This effect can be used to control the emission color of suitably structured PLED's.

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