

Quantum Efficiencies of Electroluminescent Poly(Para-Phenylenes)

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Abstract

Poly(para-phenylene) (PPP) and its derivatives with their band-gap corresponding to blue light have shown to be suitable as active layers in Light Emitting Diodes (LEDs). One important factor for the efficiency of these devices is the photoluminescence quantum yield of the active layer. Intermolecular effects in the layers (excitation energy transfer (EET), self-quenching and excimer-formation) lead to a decreased quantum yield in solid state compared to solutions. We investigated the photoluminescence quantum yields of para-hexaphenyl and several PPP-type ladderpolymers in solution and solid state. We report on the measured quantum yields (up to 85% in solution and 30% in solid state) and discuss the occurring quenching mechanisms.

1 Introduction

Compared to inorganic materials, conjugated polymers provide several advantages for the use in electro-optical devices. Their band-gap can be tailored by chemical modifications to the desired wavelength [1], [2]. Conjugated polymers are easier to process and several methods for the preparation of thin films have been proposed. Low-molecular oligomers like p-hexaphenyl can be evaporated on suitable substrates and give highly crystalline films with defined optical properties [3]. Another method is the use of soluble precursor-polymers that can be casted or spin-coated on the desired substrate and after heating the film is converted to the conjugated polymer [4], [5]. By alkylating the backbone of insoluble conjugated polymers one can obtain materials that are soluble in many organic solvents like toluene or dichloromethane. In the case of PPP these sidegroups lead to a twisting of adjacent phenyl-rings. Torsion about inter-ring bonds decreases the conjugation length [6] and soluble PPP therefore loses its semiconducting properties. One can inhibit inter-ring twisting by incorporating the conjugated backbone in a rigid, ladder-type structure where four C-atoms of each phenyl-ring are connected with neighbouring rings [7,8,9]. For the use in blue LEDs [4, 10] the limiting factors are the lifetime of the devices and the overall efficiency of the used active layers and interfaces. Tsutsui and Saito [11] proposed the following formula for the efficiency of a LED-device

$$\eta_{\Phi} = \gamma \eta_F \eta_r$$

where η_{Φ} is the electroluminescence quantum efficiency, γ is the charge injection factor, η_F the fluorescence quantum yield and η_r the efficiency of singlet exciton formation.

2 Experimental

The photoluminescence spectra were recorded with a high resolution monochromator Jobin Yvon HR640 equipped with a

cooled Hamamatsu photomultiplier-detector R943-02 with a nearly constant sensitivity in the wavelength range between 450 and 650nm. Because of this flat spectral sensitivity the emission spectra were not corrected. For the excitation we used a 1000W Xenon lamp in combination with a Jobin Yvon double monochromator H 10 D UV. The UV-VIS absorption spectra were taken with a dispersive Perkin-Elmer λ -9 spectrophotometer. The low temperature measurements were done with a continuous flow helium cryostat Oxford CF1204.

For the determination of the quantum yield we compared the integral photoluminescence intensity to a fluorescence standard with known quantum yield (Coumarin 102 in Ethanol, $\eta_F=93\%$ [12]). The used cuvettes could hold films as well as solutions in the same geometry so that we could measure quantum yields of polymer-films relative to Coumarin in solution. The quantum yield η_F of the sample can be calculated by the following formula [13, 14, 15]:

$$\eta_F = \eta_r \left(\frac{A_s}{A_r} \right) \left(\frac{\alpha_r}{\alpha_s} \right) \left(\frac{n_s^2}{n_r^2} \right)$$

η_r is the quantum yield of the reference, A_s and A_r are the areas under the luminescence spectra, α_r and α_s denote the absorption of sample and reference, respectively and n is the corresponding refractive index. The solutions were purified by bubbling argon gas through for about five minutes to avoid quenching by dissolved oxygen. We did our measurements on five different materials (see Fig. 1): Films of p-hexaphenyl (PHP) were prepared by evaporating the powder in UHV on a quartz substrate. The PPP-type ladder polymers (LPPP) were dissolved in toluene and cast on quartz. We investigated four different LPPP derivatives. The short-chained ladder polymer (s-LPPP) has a molecular weight that corresponds to 20 phenyl-rings, the long chained polymer (l-LPPP) consists of 52 phenyl-rings along the backbone. The length of Me-LPPP corresponds to about 50 rings and the substituent at the bridging between the phenyl-

rings is a methylene group. Co-LPPP is a copolymer with LPPP-segments of different lengths.

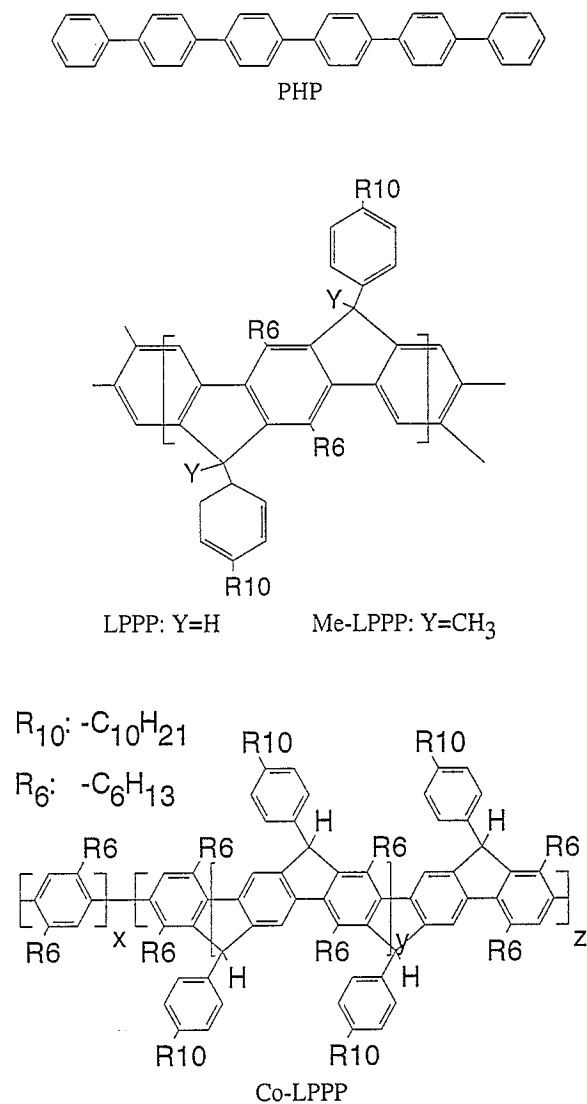


Fig.1: Chemical structure of PHP, LPPP, Me-LPPP and Co-LPPP (x:y = 50:50)

3. Results and Discussion

In table 1 we give a summary of the measured photoluminescence quantum yields η_F of LPPP, Me-LPPP and Co-LPPP in solution and film as well as of PHP in film. The solubility of PHP in organic solvents is too low [16] to measure η_F in solution. For the refractive indices of all films we assumed a value of $n=1.8$. The quantum yields in solution are all quite high, indicating that intramolecular quenching effects like internal conversion (IC) and intersystem crossing (ISC) play no important role. In films the luminescence is quenched significantly. Due to the solubility of the used materials we can investigate the influence of the molecular environment (solvent, polymer-matrix, neighbouring LPPP-molecules) on the emission spectra and the quantum yield.

Table 1
Photoluminescence Quantum Yields of PPP-type polymers

Material	η_F (solution)	η_F (film)	excitation
l-LPPP	(61±5)%	(9±2)%	400nm
s-LPPP	(72±5)%	(10±2)%	400nm
Me-LPPP	(85±5)%	(24±4)%	400nm
Co-LPPP	(84±5)%	(21±4)%	370nm
PHP	-	(30±4)%	370nm

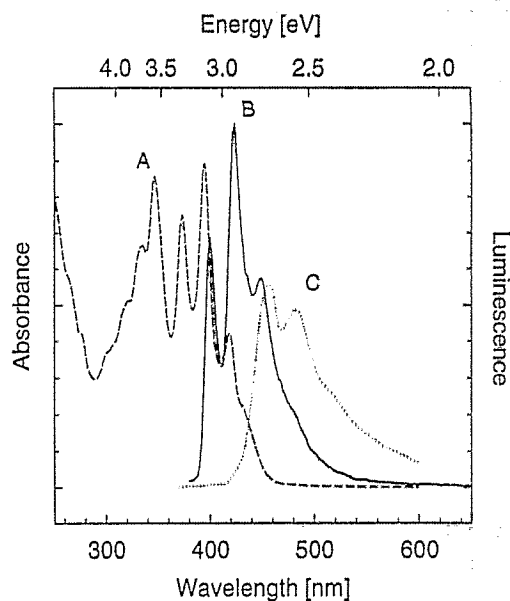


Fig.1: Absorbance (A) and photoluminescence emission (excitation 370nm, [3.35eV]) of film (C) and solution (B) from Co-LPPP

3.1 Excitation Energy Transfer (EET)

In Fig. 1 we plot the absorption (curve A) and the photoluminescence emission spectrum of Co-LPPP in toluene. The peaks are caused by the vibrational splitting of chain-segments with different conjugation lengths [17]. Each polymer-segment (ter-, penta- and heptaphenyl) causes a dominant vibronic double peak [18] at an energy corresponding to the length of the segment. In our experiment we excited the sample with a wavelength of 370nm, therefore the longest chain-segments with low-energy absorption could not absorb the incident light. In solution (curve B in Fig. 1) we observe therefore the emission of the medium-long chain-segments, and this emission has a spectral overlap with the absorption of the overall molecule. In solution the distance between neighbouring Co-LPPP molecules is too large to allow intermolecular interaction, whereas in films the distance is small enough that excitation energy transfer (EET) can occur. Mainly two facts

determine the probability P_{EET} for EET: The distance R between donor- and acceptor molecules and the overlap between fluorescence spectrum f_d of the donor and the absorption spectrum ϵ_A of the acceptor. P_{EET} can be described by the following formula [19, 20, 21]:

$$P_{\text{EET}} \propto \frac{1}{R^6} \int_0^{\infty} f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \bar{\nu}^{-4} d\bar{\nu}$$

In the case of Co-LPPP the donors are the short chain segments and the acceptors the longer segments. It is important to notice that one must distinguish between EET and self-absorption. In the case of EET donors and acceptors react through dipole or exchange interaction before the emission of the photon whereas selfabsorption occurs after photon-emission and is therefore depending on the optical density of the sample and the geometry of the experiment.

3.2 Excimer Formation

In fig.2 we plot the photoluminescence emission of a pure Me-LPPP film (curve A) and of Me-LPPP in p-(methyl-metacrylat) (PMMA) with high concentration of Me-LPPP (curve B) and low concentration (curve C). The spectra were normalized to the optical density of the films. In all three samples we observe about the same intensity of interband-luminescence in the region between 450nm and 520nm. Compared to solution in toluene this blueish emission is significantly quenched (see later). Depending on the concentration of Me-LPPP and therefore on the distance between Me-LPPP molecules we observe a broad yellowish emission from 520nm to 650nm that can be explained by the formation of excimers (excited state dimers). The formation of excimers can be found in several molecular crystals and polymers [22, 23] and was also proposed to occur in PPP [24].

3.3 Collisional Quenching

In all investigated samples (table 1) the quantum yield in films is significantly lower than in the corresponding solution. Two effects can be considered to be responsible for luminescence-quenching in films [20]: static quenching by formation of aggregates in the unexcited ground-state and collisional quenching due to interaction in the excited state.

We propose that mainly collisional quenching is responsible for the decrease of the quantum yield. The absorption spectra of LPPP films do not differ from the absorption spectra in solution (except for a small shift of the peaks caused by the dipole interaction with the solvent). This indicates that no aggregation, that is necessary for static quenching, in the unexcited ground-state takes place in films.

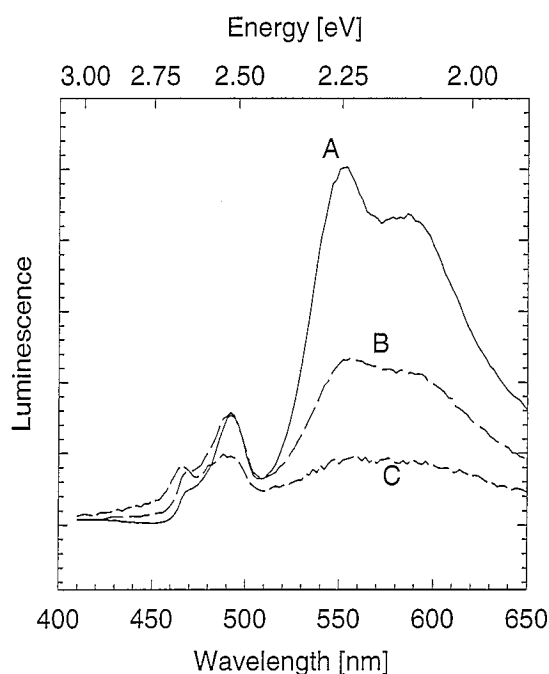


Fig.2: Photoluminescence (excitation 400nm [3.1eV]) of Me-LPPP in film (A) and in PMMA (B,C)

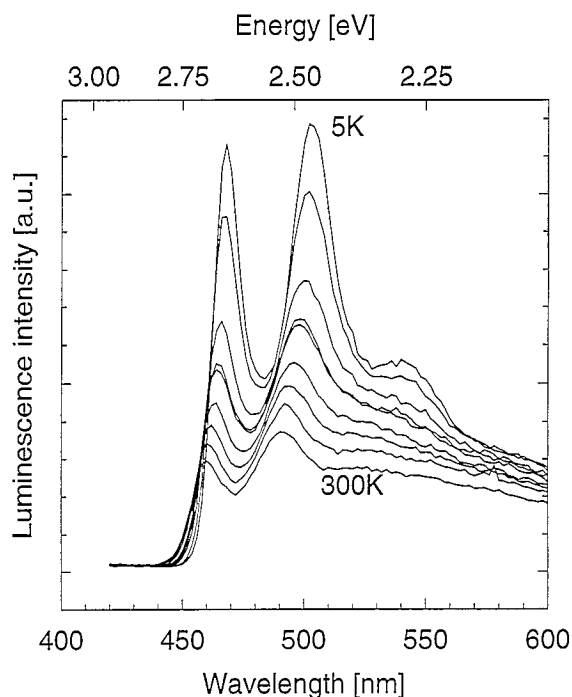


Fig.3: Photoluminescence of 1-LPPP (exc. 400nm [3.1eV]) in the temperature range between 5K and 300K

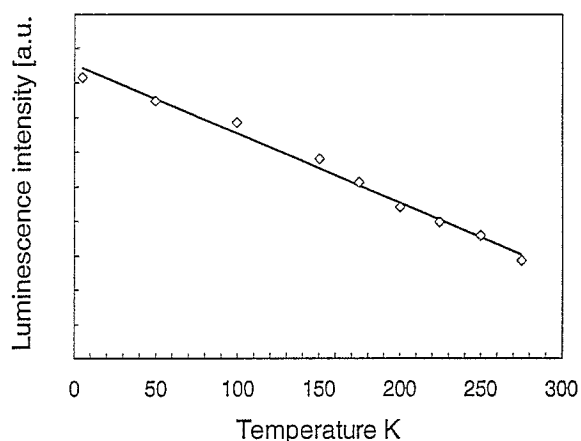


Fig.4: Integral luminescence intensity of l-LPPP depending on temperature

The temperature behaviour of luminescence in a film of l-LPPP is plotted in fig. 3 and shows that the quantum yield increases by a factor of 2.3 (see fig.4) between 300K and 5K as it is qualitatively expected for collisional quenching [20], since higher temperatures lead to higher collision-probability. For static quenching one would expect a decrease of the quantum yield at lower temperatures.

Intramolecular quenching effects like internal conversion (IC) and intersystem crossing (ISC) would lead to an Arrhenius-type temperature behaviour [25] in contrast to our measurements (see fig. 4) with a linear temperature dependence of the integral luminescence intensity. IC and ISC can therefore not explain the decreased quantum yield in films.

4 Conclusion

We have shown that intermolecular effects are responsible for the decrease of the photoluminescence quantum yield of PPP-type ladder-polymers compared to the corresponding solution. LPPP and PHP have been used as active layer in LEDs and our measurements on the photoluminescence quantum yields show that mainly the efficiency of the interfaces and the charge injection is the limiting factor for the overall performance of polymer-LEDs. We observed excimer-formation in LPPP-films and excitation energy transfers in films with large overlap between absorption and emission spectra.

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5 References

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