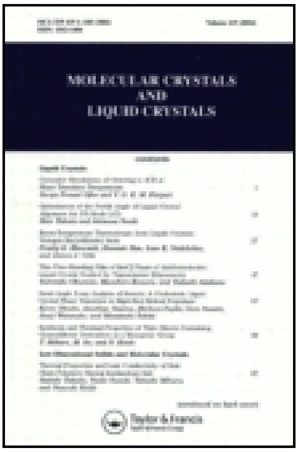

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Control of the Emission Properties of Conjugated Polymers: Trapping and Microcavity Effects

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CONTROL OF THE EMISSION PROPERTIES OF CONJUGATED POLYMERS: TRAPPING AND MICROCAVITY EFFECTS

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Abstract We report on two different approaches to modify the emission spectra of poly(phenyl-phenylenevinylene). By doping with different amounts of a laser dye, the fluorescence spectra shift to lower energies due to picosecond transfer of the excitations from conjugated segments of the polymer to the acceptor molecules. As an alternative approach we show that Fabry-Perot microcavities can be used to control and enhance the spontaneous emission of a conjugated polymer layer.

INTRODUCTION

The physics of electronic excitations in conjugated polymers is currently a matter of intense research. From the fundamental point of view the nature of the elementary excitations and their relaxation dynamics is of large interest. It is debated how disorder and Coulomb effects modify the quasi one-dimensional nature of the electronic excitations which are delocalized along the polymer backbone. The technological interest in this field is driven by the promising prospects for light-emitting devices based on conjugated polymers. Large progress has been made since the first observation of electroluminescence in poly(p-phenylenevinylene) (PPV) in 1990[1]. Besides the growing understanding and the subsequent improvement of the electronic properties of the diodes [2, 3, 4],particular interest was devoted to the control of the emission spectra. Recently, Vestweber et al.[5] have shown that emissive layers in organic LEDs can be prepared by blending a non-conjugated binder with either a soluble conjugated polymer or with oligomers of PPV. A straightforward extension of this concept is to use composite systems of oligomers or dye molecules and a soluble conjugated polymer as optically active species in such devices.

An alternative but completely different approach to the control of the luminescence spectra of organic LEDs is to design an optical confinement of the luminescent layer in order to take advantage of microcavity effects[6, 7]. Since the fabrication of suitable thin films of conjugated polymers and related materials is easily feasible, this concept is of large importance for electroluminescent devices based on this class of materials.

From a fundamental point of view the above mentioned systems are particularly interesting since they are model systems for two different physical phenomena:

1. Energy transfer processes of singlet excitations may be studied in mixtures consisting of organic dye molecules and conjugated polymers. The composite system of the organic dye and the conjugated polymer is a donor-acceptor system, where the PPPV plays the role of a donor with significant inhomogeneous broadening due to the disorder present in amorphous polymers.
2. In organic microcavities[13, 14], the alterations of the radiative transition probabilities and the emission pattern due to the optical confinement can be nicely studied since the preparation of such systems is easier as compared to their anorganic counterpart. Additionally they exhibit high luminescence quantum efficiencies at room temperature.

Here we present the results of an experimental study of these phenomena occuring in structures based on the soluble conjugated polymer poly(phenyl-phenylenevinylene). We find that mixing small amounts of dye molecules into the polymer blend leads to a concentration dependent redshift of the emission spectra. This effect is accompanied by a faster decay of the conjugated polymer luminescence. The results are attributed to efficient transfer of neutral optical excitations from the initially excited conjugated polymer states to the dye molecules. The luminescence dynamics in these systems is determined by an interplay between energy relaxation within the electronic states of the conjugated polymers and trapping at fluorescent traps and quenching sites.

In a microcavity the luminescence properties of PPPV change drastically. We show that an optical microcavity with PPPV as the luminescent material not only acts as an intrinsic spectral filter but also leads to a drastically enhanced emission within a spectral window determined by the optical mode of the cavity.

EXPERIMENTAL

The experiments on the composite samples were performed on thin films cast from a solution of PPPV and polycarbonate(PC) solved in chloroform in a weight ratio of 20:80. Different amounts of a commercially available laser dye (DCM) were introduced into the solution prior to preparation of the films. A thin film of DCM in PC was also prepared for comparison. The PPPV-microcavity samples were prepared via spin coating a thin layer on a dielectric mirror with high reflectivity near the emission maximum of PPPV and low reflectivity around 3.1 eV allowing for effective excitation in this spectral range. The sample thickness d was chosen to be about 180 nm which results in a $\lambda/2$-cavity for wavelengths within the emission band of PPPV. As the backside mirror we use a thin evaporated Al-layer.

For time-integrated and time-resolved measurement of the photoluminescence spectra the samples were excited with the frequency doubled output of a femtosecond mode-locked Ti:sapphire laser. The laser-pulse duration was 150 fs at a photon energy of 3.1 eV. The luminescence was dispersed in a 0.64m monochromator with a Si-diode array for the time-integrated detection and a streak-camera with 30 ps time resolution for the time-resolved studies. The experiments were performed under low intensity conditions in order to avoid sample degradation and nonlinear effects. The samples were kept in a He-flow cryostat during the investigations. Fluorescence excitation spectra were taken with a tunable monochromized tungsten lamp as excitation source.

RESULTS AND DISCUSSION

Dye Doped Samples

Fig. 1 shows the low temperature luminescence spectra of PPPV/PC blend samples doped with different concentrations of DCM. The doped samples the spectra exhibit contributions from both the polymer and the dye fluorescence. Depending on the concentration one of the two components becomes more prominent. The spectral maximum shifts by more than 200 meV towards lower energies for higher concentrations of DCM. The origin of the two component fluorescence spectra can be attributed either to direct excitation of both species or dynamic excitation transfer from one species to the other one.

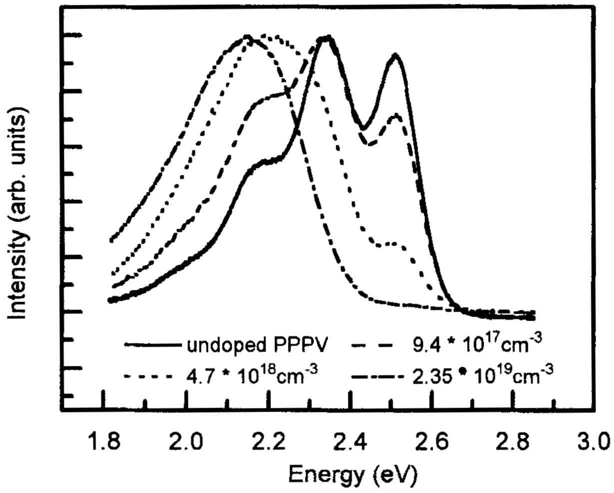

Figure 1: Low temperature fluorescence spectra of the polymer blend samples consisting of 20% PPPV in PC doped with DCM. The numbers refer to the different amounts of DCM doped into the samples. The excitation photon energy was 3.1 eV.

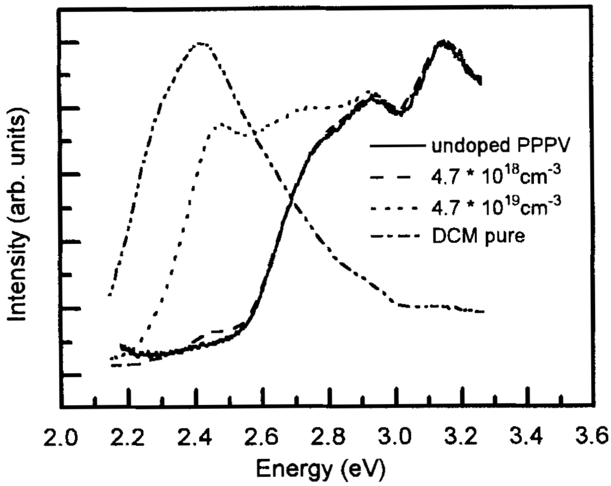

Figure 2: Fluorescence excitation spectra of PPPV/PC samples with different concentrations of DCM. The fluorescence was detected at 2.05 eV.

Evidence for a transfer of the excitation from the initially excited conjugated polymer states to the dye molecules is given by the fluorescence excitation spectra depicted in Fig. 2. Here the fluorescence was detected at an energy, where the luminescence is dominated by the contribution from DCM. Besides for the sample with the highest concentration of DCM, the structure of the excitation spectrum is very similar to the absorption spectrum of PPPV. Thus we have to conclude that the absorption of a photon by the conjugated polymer is followed by a rapid excitation transfer to the dye molecules which then subsequently emit light.

Time-resolved luminescence spectroscopy allows us to directly monitor the relaxation of photoexcitations from the initially excited PPPV to the DCM-molecules. Fig. 3 shows the time-resolved luminescence traces taken at the high energy side of the PPPV luminescence band. Here we present data for a detection photon energy of 2.53 eV. This energy is close to the center of the purely electronic $S_1 \rightarrow S_0$ emission band of PPPV. The luminescence decay is in all cases nonexponential. Even in the undoped PPPV sample the 1/e decay time is only 270 ps, which is due to dominant nonradiative processes. As pointed out in previous work[8], trapping of excitations into quenching sites is the dominant nonradiative process in PPPV. By doping with an acceptor molecule the trapping of excitations is enforced in a controlled manner. As seen in Fig. 3, the decay of the PPPV-luminescence becomes gradually faster for

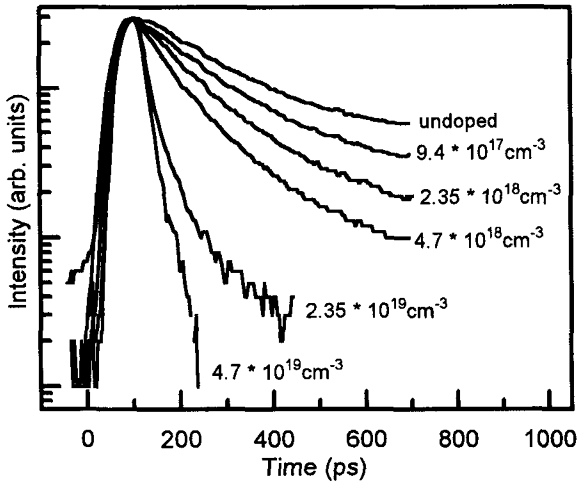

Figure 3: Time resolved luminescence traces detected at 2.53 eV for different concentrations of DCM doped into a polymer blend consisting of 20 % in PC. For excitation we have used 150 fs laser pulses at 3.1 eV.

higher dopant concentrations. Ultrafast energy transfer on a time scale comparable with the time resolution of our setup (~30ps) is observed at a concentration of $2 \cdot 10^{20} cm^{-3}$.

A quantitative description of the observed phenomena has to include different relaxation processes which occur after photoexcitation. After photoexcitation into the vibronic progression, rapid subpicosecond vibrational relaxation leads to a statistic occupation of the inhomogeneously broadened electronic density of states (DOS) of the conjugated polymer.[9] Thereafter the neutral excitations at high energies undergo hopping transfer to energetically lower lying neighboring states of the same chain. This process occurs also on a time scale faster than the time resolution of our experiment. For the discussion of the subsequent dynamics investigated here at least four different processes have to be considered. Spectral relaxation involving inter-chain hopping is of importance in samples with a sufficiently high density of conjugated segments. Trapping of neutral excitations into so far unidentified traps can quench the luminescence significantly. Furthermore, separation of electrons and holes also may lead to a reduction of the luminescence intensity. This process can be either intrinsic due to the disorder mediated dissociation of neutral excitations or extrinsic due to traps which act as electron acceptors as e.g. in the case of C_{60} doped into conjugated polymers[10, 11]. The intrinsic lifetime for radiative recombination in PPPV is on the order of 1 ns which is much longer than the decays observed here. Thus we conclude that the decays measured here are dominated by trapping into either nonradiative quenching sites or fluorescent dye molecules. For a concentration of $4.7 \cdot 10^{18} cm^{-3}$ the luminescence of the doped sample decreases twice as fast to 1/e of the initial value as compared to the undoped PPPV-sample. Assuming a random spatial distribution, the typical distance between the acceptor molecules in this sample is 6 nm. This is a reasonable value for an effective Förster-transfer where a conjugated segment of the polymer acts as the donor and DCM as the acceptor. However, since the conjugation length is of the same order, higher order multipolar interactions may contribute to the coupling. This study also allows for an estimation of the trap density in PPPV. Assuming that the transfer does not depend drastically on the nature of the acceptor sites, we conclude that the trap density in the undoped samples is also about $5 \cdot 10^{18} cm^{-3}$cm. This value is in good agreement with recent results achieved by modelling the ultrafast fluorescence dynamics in conjugated polymers[12].

Conjugated Polymer Microcavities

An alternative approach to modify the emission spectra of conjugated polymers, is to use Fabry-Perot microcavities. Fig. 4 depicts the time-integrated emission spectra of the PPPV-microcavities and two reference samples. For comparison we have

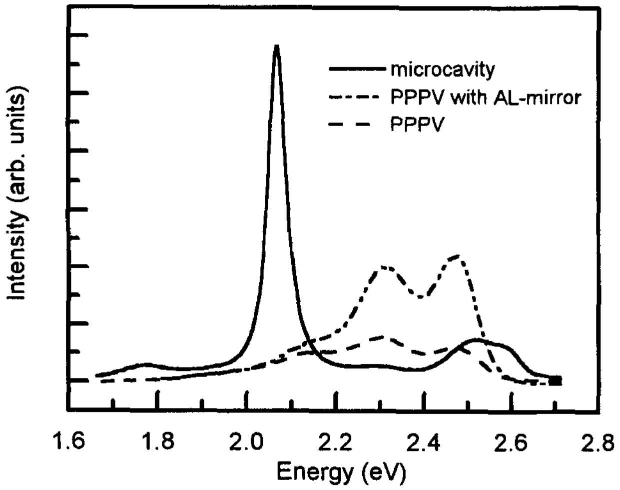

Figure 4: Time integrated fluorescence spectra of the PPPV microcavity compared with a film of the same thickness with and without backside Al-mirror. The excitation energy was 3.1 eV

measured the luminescence of a PPPV-film of the same thickness spin coated on a glass substrate. The sample was partially coated with an Al-layer in order to measure the emission with and without a backside mirror. In all cases the spectra were measured under the same excitation conditions. The exciting laser beam penetrated through the dielectric mirror and the glass substrate, respectively. The luminescence was detected at the same side of the sample. The most obvious difference is that the emission spectrum of the microcavity is restricted by the cavity resonance to a narrow spectral range with a full width at half maximum of 50 meV. Additionally, the intensity at this spectral position is considerably enhanced as compared to the sample without cavity. This demonstrates that control and enhancement of spontaneous emission in thin conjugated polymer films can be achieved in this rather simple geometry. A straightforward extension is to use this approach for LEDs with tailored emission properties. From a technological point of view the use of spin coated layers in microcavities may be advantageous as compared to Langmuir-Blodgett films[6] or sublimated organic layers. However, further investigations are required to understand in detail the modification of the radiative recombination by the optical confinement.

CONCLUSIONS

We have demonstrated two ways of changing the emission spectra of poly(p-phenylenevinylene) drastically. Doping with different amounts of a dye molecule leads to efficient transfer of photoexcitations from the conjugated polymer to the acceptor. For the highest concentration the transfer time decreases to values smaller than 30 ps. By variation of the concentration the time integrated emission spectra can be gradually shifted over 200 meV.

An alternative way to control the spontaneous emission of a conjugated polymer is the use of a microcavity. Spectrally narrow spontaneous emission with enhanced intensity was observed.

Both ways of modifying the emission spectra may be applied for spectral tuning of organic electroluminescent devices.

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