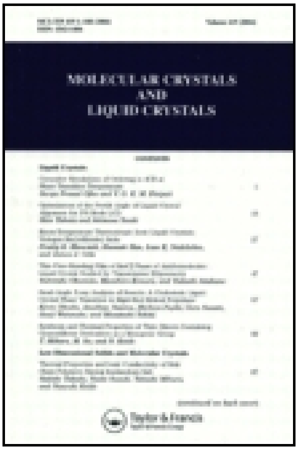

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Magnetic Field Effect as a Test for Effectiveness of the Light Emission at the Recombination of Injected Charge Carriers in Polymeric Semiconductors

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The electroluminescence (EL) of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) under DC magnetic field has been investigated experimentally and analyzed theoretically. We have estimated the lifetime of intermediate polaron pairs and relation between rate constants of recombination of triplet and singlet polaron pairs from the changes of the EL intensity caused by the DC magnetic field. The short lifetime of the polaron pairs (about 2×10^{-10}s) in MEH-PPV has been discussed by taking the intersystem crossing in polaron pairs into consideration.

Keywords: conducting polymers; electroluminescence; magnetic field spin effect; polaron pairs; recombination of charges

I. INTRODUCTION

Double infection of charge carrier into a conjugated polymer film is known to result in the light emission that originate from singlet

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excitons formed at the recombination of charges, EL [1,2]. Organic light-emitting diodes (OLEDs) based on that phenomenon find many useful applications [3]. For choosing a proper polymer for the OLEDs it is important to understand, which part of the energy released at the recombination may be converted into the light. In a simpleminded scheme this part is 1/4 assuming that meeting of two opposite charged carriers in the singlet state is enough for producing a singlet exciton. However in organic materials with low mobility of charge carriers a new intermediate state is known to be formed at the recombination. This state is called usually as a polaron pair, and it represent two charges in a potential well formed due to their Coulomb attraction. The pairs can be in a singlet and triplet states, and what is important, their lifetime may be long enough for mutual intersystem crossing caused by a hyperfine interaction [4,5].

Figure 1 shows schematically main processes occurring in the OLEDs. One can see that because of intersystem crossing between singlet and triplet polaron pairs, initial ratio of charge meeting events in a singlet and triplet state (1 to 3) can result in a quite different ratio of the rates of formation of singlet and triplet excitons. Critical

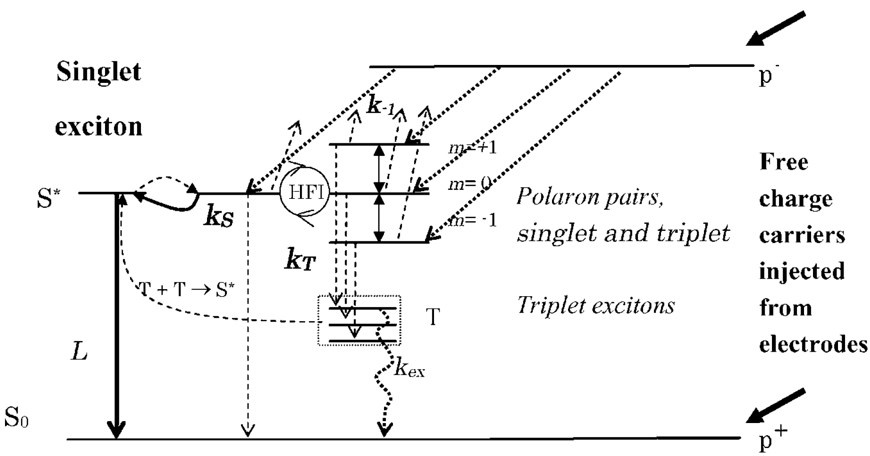

FIGURE 1 A scheme of main processes responsible for the electroluminescence at free carrier injection into a semiconducting polymer. The picture corresponds to the case of a dc magnetic field superimposed on the sample. Polaron pair's formation is shown at recombination of free charge carriers. HFI shows the mixing of magnetic substates of polaron pairs by a hyperfine interaction. Arrows between sublevels of triplet polaron pairs correspond to microwave induced resonant transitions in a magnetic field.

parameters here are rate constants of recombination of charges inside the pairs of different multiplicity, k_S and k_T. Depending on relative values of these rate constants, one can imagine the quantum yield of the electroluminescence, determined as a ratio of a number of recombination events to the amount of singlet exciton produced.

$QY = k_S/(k_S + 3k_T)$, to change from 1 to 0, being equal to 0.25 at $k_S = k_T$. Of course it will be so if the total lifetime of the pair τ is long enough to permit the pair spin evolution to occur under the action of hyperfine interaction. The time needed for spin evolution is of the order 5 ns.

Thus, it becomes important and interesting to estimate relative values of these rate constants and the lifetime of the pairs in order to get knowledge about perspectives of using any particular polymer in OLED devices.

In the present work we are using the Magnetic Field Spin Effect on polaron pairs in order to estimate these parameters. As observables we are using here changes of the electroluminescence intensity, when working with double injection of carriers into an polymer film.

The question about relative values of the rate constants was considered in the literature [6,7] being based on experiments with light excitation induced polaron pairs performed by Indirectly Detected Magnetic Resonance (original name of it is Reaction Yield Detected Magnetic Resonance-RYDMR [8]). It deals with microwave induced resonant transitions between magnetic spin sublevels of polaron pairs in the triplet state in a DC magnetic field. These transitions are shown in the Figure 1 by arrows between magnetic sublevels of triplet polaron pairs. Resonance induced changes of the photoluminescence (PLDMR), photoconductivity (EDMR), photoinduced absorption (ADMR) are usually measured, and the problem consists in finding a mechanism connecting resonant transitions in the pairs and the changes of observables.

Interpretation of experimental data depends heavily on the model used for describing formation of polaron pairs.

Sequence of events used in the model applied has a crucial role as far as it determines the population of the pair sublevels. If the pairs are produced first at the light absorption they conserve the spin state of the precursor that is usually in the singlet state. But if the pairs are a result of free charge carrier recombination they can be as in the singlet, and in triplet states. Interpretation of experimental results may lead to quite different conclusions for different models. As an example one can mention recent publications devoted to determination of rate constants for charge recombination inside the polaron pairs k_S and k_T, which can be in the singlet and triplet states [6,7]. Here, experimental data can lead to the conclusion that $k_S > k_T$ if it is assumed that at the photoexcitation of a polymer polaron pairs are produced in the process of recombination of free charge carrier. But the same data would result in reciprocal relation, $k_S < k_T$, if the model with primary photogeneration of polaron pairs is applied. The paper [9] is devoted to detailed discussion of that problem. A task of the present work is to supply additional experimental data based on Magnetic Field Spin Effect that can permit to estimate this important relation.

II. METHODICAL

A scheme of energy levels of polaron pairs in a magnetic field and main processes within the pairs are shown in Figure 1. Pairs are produced from their precursors in the same spin state as precursors had. During lifetime of the pair (a typical lifetime is of the order of nanoseconds) a spin evolution takes place, and different substates of the pair become mixed with each other due to intersystem crossing induced by a hyperfine interaction of electron spin with magnetic moment of nucleus (protons). For mixing, energy levels of polaron pairs must have the same position, so in zero magnetic field all four sublevels are mixed, and in an external magnetic field, which is more strong than hyperfine field, mixing of the singlet substate with one triplet substate m = 0 is only possible. This case is shown in the Figure 1.

We are going to see changes in the intensity of electroluminescence appearing as a result of recombination of free charge carriers. As it follows from the Figure 1, in zero magnetic field the quantum efficiency of the fluorescence is

$$QE_0 = \frac{k_S}{k_S + 3k_T + 4k_{-1}}$$

In a high magnetic field

$$QE_B = \frac{k_S}{2(k_S + k_T + 2k_{-1})}$$

Relative change of the fluorescence intensity at the switching on the magnetic field

$$\frac{\Delta L}{L} = \frac{QE_B - QE_0}{QE_0} = \frac{k_T - k_S}{2(k_S + k_T + 2k_{-1})} \tag{1}$$

Thus, the sign of relative changes of the recombination fluorescence intensity permits estimating the ratio k_S/k_T.

III. EXPERIMENT AND DISCUSSION

We have used the next electroluminescent device structure: ITO/PEDOT:PSS/MEH-PPV/MgAg. EL corresponded to fluorescence of MEH-PPV, and the total intensity L of EL was measured distantly at zero magnetic field and at the superimposed DC magnetic field within the range from zero to 2500 G. Temperature of the sample was 288 K.

The results obtained at different voltages are shown in the Figure 2. Relative changes of the intensity $\Delta L/L = (L_B - L_0)/L_0$ are plotted against magnetic field strength B. These results show that the luminescence changes are positive and becomes smaller at higher voltage applied. The positive change may serve as evidence that $k_T > k_S$ according to formula (1). A very important feature of the results consists in leveling off of the curve at magnetic fields B, which are much higher than an hyperfine magnetic field caused by hydrogen nuclei. The latter are expected to be of the order 10 G. But a half saturation field $B_{1/2}$ lies near 250 G. We suggest rationalizing that result as a

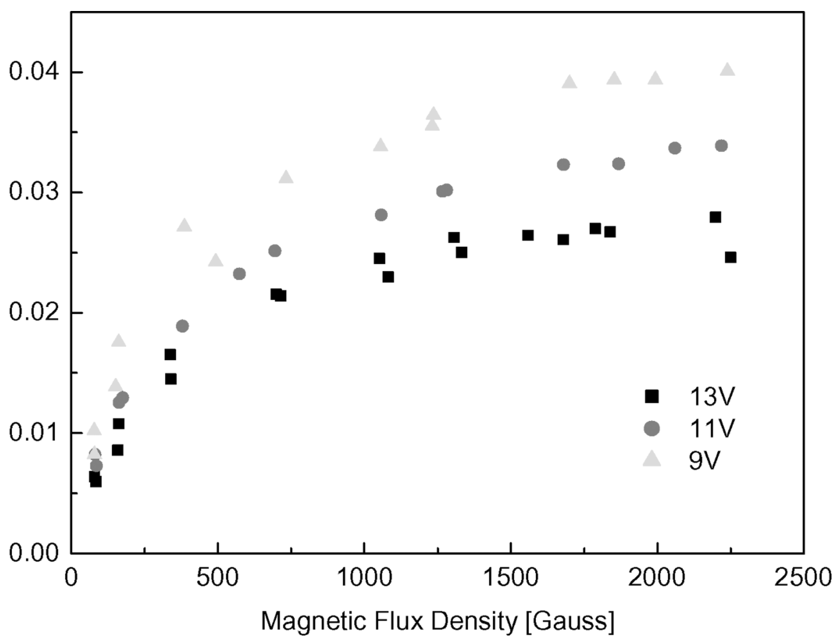

FIGURE 2 Dependencies of relative changes of the fluorescence light intensity on the DC magnetic field strength within the range from 0 to 2250 G. Different kinds of points correspond to voltages applied to electrodes indicated.

sequence of a short lifetime τ of polaron pairs produced at the recombination of injected charge carriers. By applying the uncertainty relation $g\beta B_{1/2}\,\tau = h/2\pi$ we arrive at the next estimate of the lifetime: $\tau = 2 \times 10^{-10}$ s. Such a short time is not enough for effective intersystem crossing inside the polaron pair. It explains why splitting the triplet state of the polaron pair changes the intensity of EL for a few percents only: formation of the singlet pairs at the recombination leads to formation of EL excited state mainly, and only a small part of the pairs has a chance to be converted into the triplet pairs. Taking into account the value of Magnetic Field Spin Effect at saturation (MFSE)-max one can estimate the number of EL photons per one recombination event as $QY = 1/4 - (\mathrm{MFSE})_{\max} 3/2 \approx 0.2$.

IV. CONCLUSION

Using changes of the electroluminescence intensity caused by the DC magnetic field permits estimating the lifetime of intermediate polaron pairs and relation between rate constants of recombination of triplet and singlet polaron pairs. Short lifetime of the polaron pairs (about 2×10^{-10} s) makes intersystem crossing in polaron pairs not very essential.

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