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Role of spin states in the process of electron energy transformation in P3HT films, doped KI salt

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Role of spin states in the process of electron energy transformation in P3HT films, doped KI salt

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Abstract. Influence of KI salt on the spectral-luminescent properties of polymer films of P3HT has been investigated in this work. Addition of KI doesn't lead to significant changes in optical density of the polymer films, but significantly changes the intensity and lifetime of the luminescence of P3HT. Adding KI reduces the lifetime of P3HT luminescence. Growth of the luminescence intensity occurs at a low concentration of KI and its quenching occurs at the high concentrations. A significant increase in the electrical resistance of the films takes place by adding of the KI. Type of magnetic effects on the photoluminescence of P3HT depends on the concentration of KI. Changes in the magnetic effect in P3HT-KI films are connected with increase in the concentration of triplet states in the polymer.

1. Introduction

Research of electronic processes in organic semiconductors actively conducting these days [1]. This interest is due to the great potential of practical application of such materials to create the elements of molecular electronics [2], elements for optoelectronics [3], in particular organic light-emitting diodes [4], organic photovoltaic elements [1], etc.

One of the possible ways to improve the efficiency of the polymer solar cells could be an increase in the singlet-triplet conversion in polymers. This can be achieved by changing the spin-orbit interaction, using external heavy atom effect [5]. It was shown earlier [6], that by adding KI-salt in epy polymer film of poly(3-hexylthiophene-2,5-diyl) (P3HT) occurs an increase of the intersystem crossing between electronic S_1 and T_1 states of the polymer. This represents a significant contribution to the excited triplet states of P3HT polymer of the organic solar cell in the process of transformation of light energy into electrical energy.

However, growth concentration of T_1 states in the polymer complicates the nature of the transformation of energy in the cells. Therefore, the mechanism of the effect of external magnetic field on the processes of the electron energy transformation in P3HT polymer films is not yet clear. The way to clarify the electron energy transformation in the organic semiconductor polymer could be the effect of the external magnetic field on the photoluminescence, electroluminescence and an electric current in the polymers.

The formation of excitons, polarons and bipolarons take place in the polymers with optical excitation [7,8]. Magnetic field (MF) can influence a number of processes involving these electronic

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states. The MF influences on the interaction of triplet-polaron [9], on the conversion process of electron-hole precursor pairs [10] and on the spin conversion bipolaron precursor pairs [11]. It is necessary to take into account that the main change in the luminescence intensity and/or current can occur at small values of the induction of magnetic field (B), so-called low field effect, and at higher B - high field effect [8]. If the low field effect is usually associated with the hyperfine interaction [12], the high field effect can be caused by a number of different mechanisms, in particular triplet-triplet annihilation [13]. Therefore it is necessary to conduct comprehensive research for a deeper understanding of the electron energy transformation processes in semiconductor polymers. For example, in [6], we investigated the effect of potassium iodide salts on the photoluminescence and photovoltaic properties in the P3HT-PCBM organic solar cells. This article presents the results of studies of an effect of external magnetic field on the photoluminescence films of P3HT, doped with the KI salt. The results of the studies suggested a possible mechanism for the effect of the MF on the photoluminescence films of P3HT-KI.

2. Experiment

The P3HT polymer films based with the inorganic impurities additives of KI were prepared for study of spectral-luminescent properties of the polymer composites. The impurity concentration in the film of P3HT is in the range from 0.05 to 1 weight percent from mass of the polymer. Methods of preparing the polymer films P3HT–KI, is given in [6].

Registration the absorption spectra of the films was carried out using a spectrophotometer Cary 300. The excitation and luminescence spectra of the films were measured on a fluorescence spectrophotometer Cary Eclipce.

The kinetics of fluorescence of polymer films was measured using a pulsed spectrofluorometer with picosecond resolution and recording mode with time-correlated photon counting (Becker & Hickl). Fluorescence excitation of samples was carried out using a pulsed semiconductor laser with a wavelength of λgen = 488 nm and pulse width at half maximum of τ = 80 ps.

The effect of the external MF on the kinetics of a fast luminescence in the polymer films was measured by the pulsed spectrofluorometer Becker & Hickl. A neodymium magnet was used for the formation of the MF. Method of measuring of the MF effect on the luminescence kinetics of P3HT is described in detail in [6].

3. Results and discussion

Study of the spectral-luminescent properties of P3HT-KI films was carried out. The absorption spectrum shows a broad absorption band with the maximum on 520 nm and a shoulder at 600 nm (Figure 1, a). The adding impurities in the film leads to a slight change in shape of the absorption spectra on the short-wavelength part. The long-wavelength part of the spectrum is practically unchanged.

From the absorption spectra of the polymer films an energy value of bandgap (Eg) P3HT was determined by the addition of the inorganic impurities. To determine the width of the bandgap is plotted in the coordinates eV and $(A*hv)^2$. The bandgap is determined by the intersection of tangent to the curve of the absorption film and the ordinate axis corresponding to the energy of the absorbed light [14]. Results of determining the value of Eg are listed in Table 1. These results show that the inorganic impurity practically doesn't effect on value of the polymer bandgap. No change in the bandgap indicates a small effect KI impurity on structural and energy characteristics of P3HT film.

Influence of KI impurities on the photoluminescence spectra of the composite films is shown in Figure 1, b. The addition of KI results decreases an intensity of emission at 700 nm, compared with the intensity of emission at 650 nm. Low concentration adding of KI leads to an increase in the intensity of luminescence of the polymer (Figure 2). When the impurity concentration KI in the polymer was 0,5 %, the luminescence intensity is 3.5 times higher than from pure P3HT film. Further growth of KI concentration in the polymer films leads to a significant drop in light intensity [6].

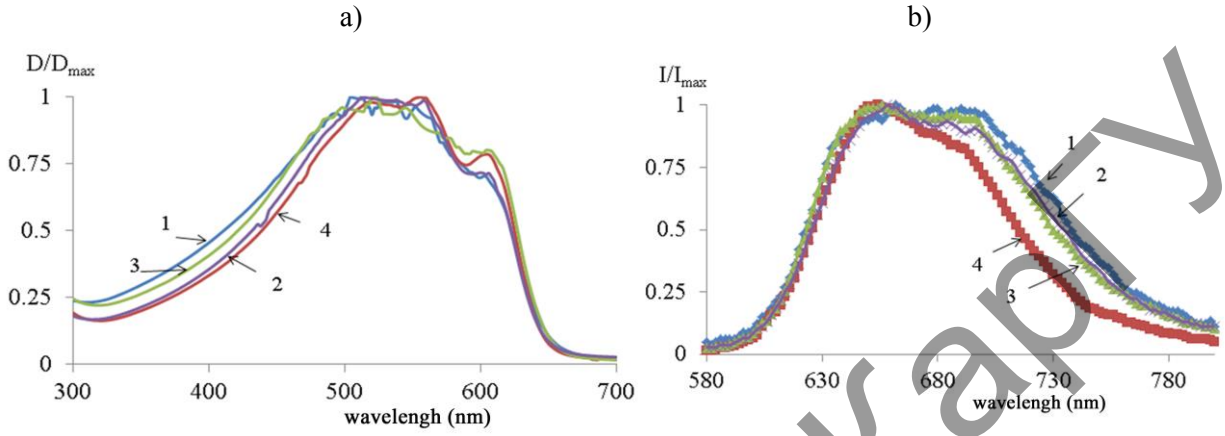

Figure 1. Relative absorption (a) and luminescence spectra (b) of P3HT-KI films. The concentration of KI impurity in the film: 1- 0; 2- 0,05 %; 3- 0,1 %; 4- 0,5 %.

Table 1. Influence of KI impurities on energy, fluorescent, electrical characteristics, and the magnetic effect in the composite films P3HT- KI

Samples	Value of bandgap (eV)	Lifetime of luminescence, τ, ps	Specific resistance ρ, Ω*cm	g_{max}(B) (%)
P3HT	1,875	460	$2,2*10^6$	+ 24 %
P3HT–KI 0,05 %	1,89	439	$4,5*10^8$	- 70 %
P3HT–KI 0,1 %	1,88	443	$4,5*10^8$	- 30 %
P3HT–KI 0,5 %	1,90	382	$1,1*10^9$	+ 30 %

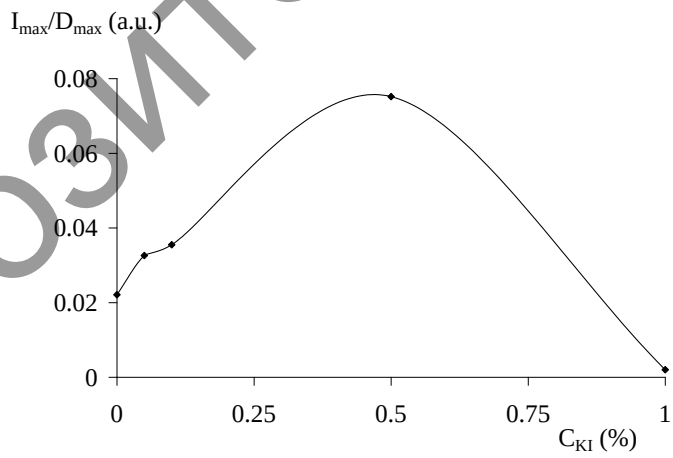

Figure 2. Dependence of the luminescence intensity of P3HT films from the KI concentration.

Kinetics of luminescence measured for P3HT-KI films in the nanosecond range. Signal registration is made at the maximum of the luminescence spectra (~ 650 nm). Lifetimes of luminescence (τ) was calculated from the linear portion of the logarithmic curve for various samples (Table 1). Maximum reduction in the lifetime observed for P3HT–KI film with the highest concentration of KI impurity. This behavior lifetime of luminescence indicates the dynamic nature of quenching of the excited

singlet state polymer S_1. The most likely cause is the increase of the rate of intersystem crossing conversion from S_1 to T_1 state of the polymer [15].

Increasing of intensity luminescence at the low concentrations of KI and it reduction at the high additions of the impurity in the films shows a difficult influense of the heavy atom effect on the electron energy transformation in P3HT film.

Also measured influence of KI on an electrical resistance of P3HT films (Table 1). Measurement of the resistance on samples with ITO/P3HT/Al layers. Thickness of the polymer layer was constant. Control of the thickness implemented witch electron microscope. A contact area of the cells was 0,1 см^2. As it can be seen from the data shown in Table 1, KI addition leads to increase of electrical resistance of P3HT films. Qualitative assessment of the effect of the bandgap on a concentration of charge carriers was cited in formula [16]:

$$n_i^2 \sim \exp\left(-\varepsilon_g / kT\right) \quad (1)$$

Assessment of impact of the bandgap on the concentration of the charge carriers showed, that changing the band gap from 1.875 to 1,9 eV may lead to changing of concentration own of a free charge carriers in 2 times. While the resistance changes by 3 times of order of magnitude. Therefore, change of the resistance of films with KI addition is not connected only with change of the bandgap of the films.

More precisely, the mechanism of the effect of heavy atoms on photophysical processes in composite films P3HT- KI can be determined from measurements of influence of the external magnetic field on the kinetics of luminescence.

Measurements showed that the magnetic field affects on the intensity of the luminescence both pure P3HT film and P3HT-KI film. There is a time-dependent magnetic effect (Figure 3). As shown in [17], an external MF doesn't affect on the luminescence films of ITO/P3HT/Al. At the same time, in work [18] was observed effects on the magnetic photoluminescence of P3HT films with presence of oxygen. The appearance of the magnetic sensitivity explained by the appearance of oxygen-induced charge transfer complexes in the films of P3HT. The magnetic effect on P3HT photoluminescence observed in our work associated with formation of charge transfer complex in the presence of oxygen molecules. Type time dependence *g(B)* for P3HT film indicates on high rate of occurrence of the magneto-sensitive stages of transformation of electronic energy. Having high speed means that triplet state is not a major in formation of the magnetic effect in film of pure P3HT.

In the case of adding KI impurity occurs change of sign of magnetic effect and sharp increase of intensity of *g(B)* (Figure 3, table 1). With increasing concentration of KI decreases the value of *g(B)* and then sign of magnetic effect of the *g(B)* returns to plus.

Similar change of the sign of the magnetic depending on the current observed in [19]. In this work current density through polymer of film P3HT $i \approx 10^{-2}$ А*см^2 was critical. Above this current density the magnetic effect on the conductivity becomes positive and with lower value of i – negative. Change in magnetic effect explained by increasing of concentration of triplet excitons (N_T). The change occurred when the same concentration of triplet excitons and holes (N_p) in the polymer ($N_T \approx N_p$).

It should be noted that external magnetic field produces the opposite effect on the electrical conductivity and the photoluminescence in the polymer films. If there is a positive effect on the conductivity in the films, then there is a negative effect of the magnetic field on the luminescence and conversely.

These data in our work shows that addition of KI impurity does not lead to changes in the structure and energetics of polymer films of P3HT. Wherein increase in the KI concentration leads to an increase resistivity resistance of films. Also adding KI impurity leads to change of sign and value of magnetic effect *g(B)*.

As shown in [8, 9], the triplet state of the polymer can reduce the intensity of luminescence in the case of triplet-polaron dispersion in semiconducting polymers. So, it can be assumed that the observed magnetic effects on the luminescence in the P3HT-KI connected with triplet-polaron dispersion.

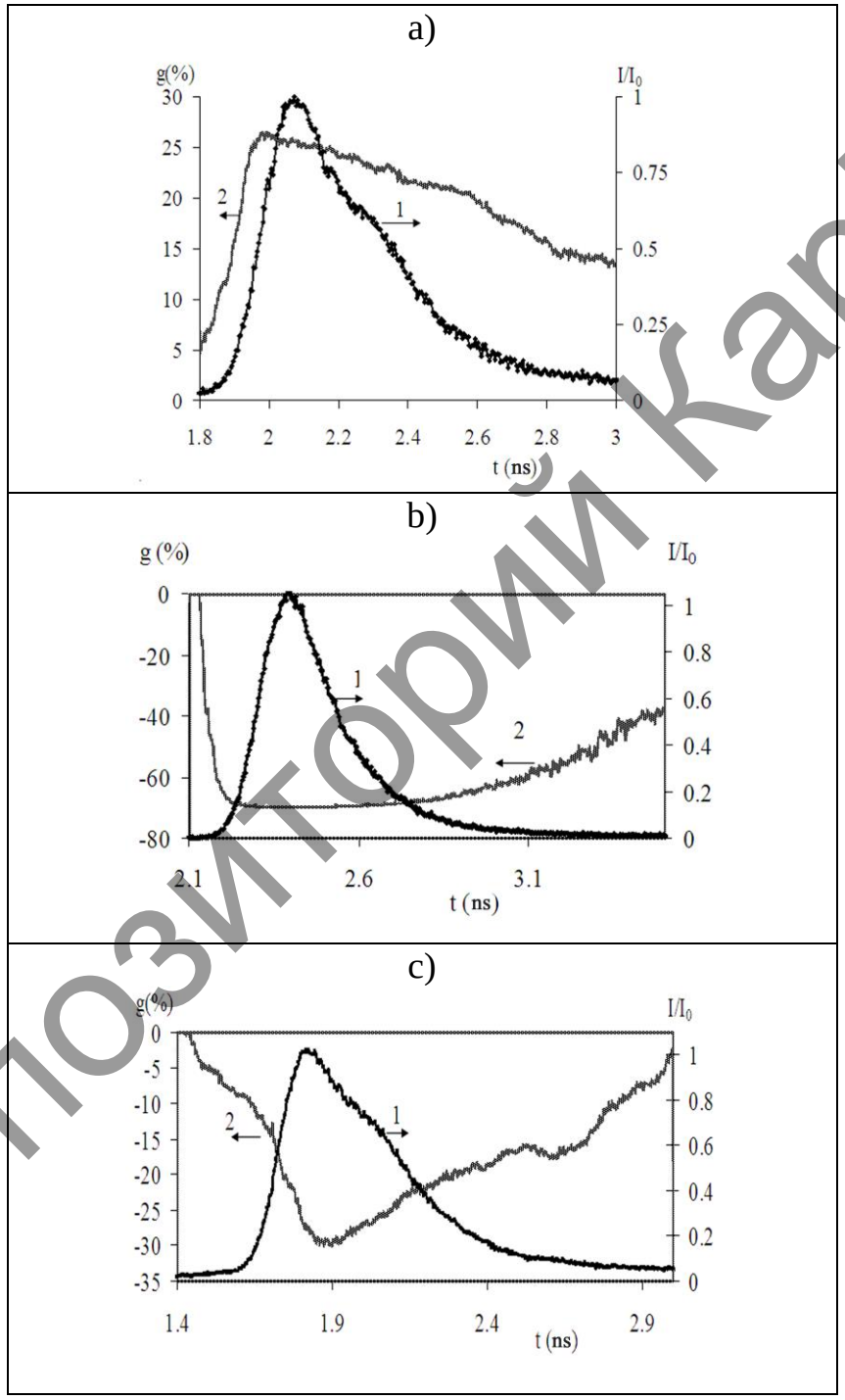

Figure 3. Kinetics of luminescence of P3HT–KI films (1) and value of magnetic field effect g(B) (2): a) P3HT; b) P3HT–KI 0,05 %; c) P3HT–KI 0,1 %

4. Conclusion

Research has shown different influense of KI impurities on the spectral-luminescent properties and the magnetic effect on the photoluminescence of P3HT semiconducting polymer. Adding impurity of KI almost does not affect on absorption spectra of P3HT films. Also there is little changes in the bandgap of the polymer. It points to the addition of KI impurity does not lead to changes in the structure and energy of P3HT. In contrast with absorption spectra, the luminescent properties of P3HT significantly changes with presence of KI. Addition of KI decreases the the lifetime of P3HT luminescence. The intensity of luminescence of the polymer depends on the impurity concentration. At a low concentration of KI occurs growth to the photoluminescence intensity and at the high concentrations (more than 1%) - decrease. Addition of KI in the film leads to increase of the electrical resistance in it. It is connected with decrease of the mobility of charge carriers in P3HT. Also character of magnetic dependence on the photoluminescence *g(B)* depends on KI concentration. With first adding of KI (0,05 %) the magnetic effect of the changes sign from plus to minus. Value of *g(B)* sharply increases to 70 %. Then with increasing of concertation of KI impurity a decrease of *g(B)* value. Then the sign of the changes from minus to plus.

The observed changes in the magnetic effect on the photoluminescence P3HT-KI films are connected with increase of the concentration of the triplet states in the polymer. When observing the negative magnetic effect *g(B)*, the main process in the film magnetically P3HT-KI is the dispersion of the polarons on the triplet states T_1 of the polymer. In this way, KI impurity can be used to control electronic processes in semiconducting polymers.

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