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Effect of potassium iodide on luminescent and photovoltaic properties of organic solar cells P3HT-PCBM

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Abstract. It has been investigated spectral-luminescence properties of polymer films, doped with potassium iodide (KI). Using of KI didn't lead to the gradual changes of optical density of polymer films and the range of band gap semiconductor polymer P3HT. The fluorescence intensity of P3HT decreased and changed by use of KI. Using of 1% KI in polymer led to decrease of fluorescence lifetime. Influence of heavy atom on photovoltaic effect of organic solar cells has been investigated. 1% of KI in polymer film led to decrease of I_{sc} and slightly decrease of U_{oc} . Investigation shows that magnetic field does not affect on photovoltaic properties of cells P3HT-PCBM. Magnetic field increased of open circuit voltage and short circuit current of solar cells with 1% of KI. Study of electrical impedance of cells revealed the magnetic sensitivity of solar cells with KI additives. The lifetime of free charge carriers increased in the magnetic field for solar cells with KI additives.

1. Introduction

Polymer solar cells based on poly [3-hexylthiophene] (P3HT) and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) could be an alternative to the traditional silicon solar cells. Efficiency of polymer cells based on P3HT-PCBM has reached 5% [1]. One of the possible ways to increase efficiency of polymer cells is increase of singlet-triplet conversion in polymers. It is reachable by changing spin-orbit interaction, by using effect of heavy atom. There is a lot of information about influence of heavy atom on photophysics organic molecules [2]. But there are not many studies of influences of external heavy atom effect on the process of transformation of solar energy into electrical energy in polymer cells.

Addition of external heavy atom in semiconductor polymers could change not only the process of photophysical reactions but also probability of creation of free charge carriers in polymer composites. However, the level of influence of external heavy atom on the electronic processes in semiconductor polymers is not thoroughly investigated.

In the present work, we report about the investigation of influence of non-organic impurity (potassium iodide) in polymer on process of transformation of solar energy into electrical in solar cells based on polymer-fulleren mix P3HT+PCBM which caused their use as a model system for investigation of electrical processes in organic solar cells.

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2. Experimental

Polymer films based on P3HT with the addition of PCBM or inorganic impurities KI were prepared for studying of the spectral-luminescent properties of polymer composites. The weight ratio was 1: 1 and 100: 1 respectively for the components in composites for mixtures P3HT-PCBM and P3HT -KI.

The glasses with conductive ITO (indium tin oxides) layer with area of 2x1.5 cm were used for the assembly of solar cells. The resistivity of ITO is 10 Ω *cm. The transmission of glass with the ITO is not less than 72 % at the maximum absorption of polymer P3HT. Solar cell was fabricated with structure ITO/PEDOT:PSS/P3HT:PCBM/Al following with method of described in detail in [4, 5].

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 Eclipse.

The current-voltage characteristics (CVC) of the cells was measured with light cell by a conductive layer (ITO) radiation of the xenon lamp power of 100 mW/cm² on simulator sunlight Solar Cell IV Measurement (Photo Emission Tech Inc.). The measurements were performed at 25 ° C. The real (Z') and imaginary (Z'') electrical resistance of solar cells was measured at impedancometry Z500PRO in potentiostatic mode for a given zero constant potential.

Neodymium magnet is used to measure the effect of an external magnetic field on the current-voltage characteristics and the impedance of cells. The magnetic field of magnet is 0.55 T.

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 $\lambda_{\text{gen}} = 488$ nm and full width at half maximum of $\tau = 80$ ps.

3. Result and discussion

Spectral-luminescent properties were investigated for the P3HT polymer films and P3HT-PCBM, PCBM-KI polymer composites. Absorption spectrum of the pure P3HT is shown in Figure 1. The broad absorption band with a maximum at 520 nm was observed for the P3HT.

Additional absorption band appears after addition PCBM in the film. This band is in the ultraviolet region of the spectrum with a maximum around 230 nm (Figure 1, a, curve 2). The optical density of the P3HT absorption decreases 2-fold compared neat a P3HT film. This is due to a decrease in amount of polymeric material in the film. Adding KI does not lead to significant changes in the optical density of the composite film P3HT-KI. There is some change in shape of the absorption spectrum of P3HT – KI film (Figure 1, a, curve 3) in comparison with the film of the P3HT (curve 1).

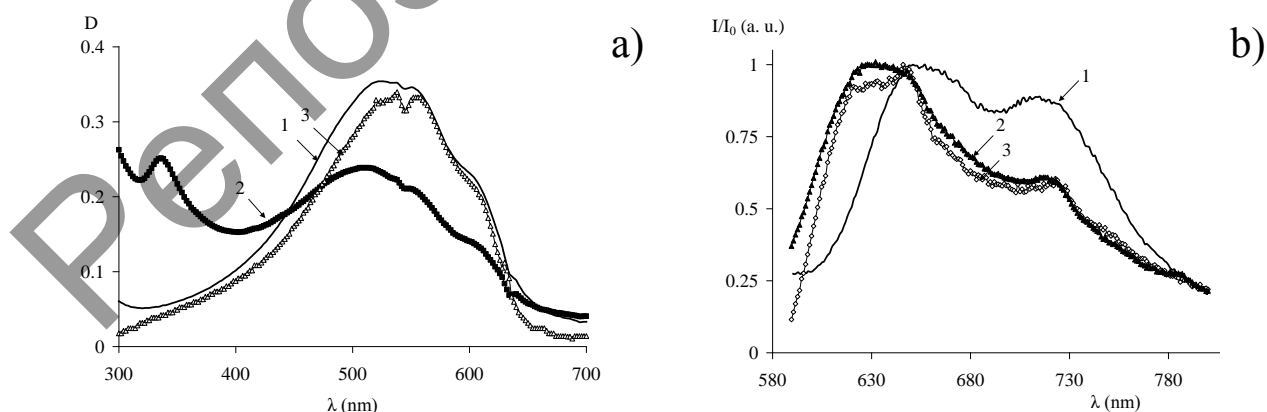


Figure 1. The absorption spectra (a) and normalized fluorescence spectra (b) of the polymer films P3HT (1), P3HT-PCBM (2) and P3HT-KI (3)

Fluorescence spectra of the P3HT, P3HT-PCBM and P3HT-KI films are shown in Figure 1, b. Broad band with a maximum at 650 nm and the shoulder at 720 nm (Figure 1, b, curve 1) is observed in the fluorescence spectrum of the P3HT film. Addition of PCBM molecules leads to a significant decrease in fluorescence intensity (10 times) and to change of the spectral curves form (Figure 1, b, curve 2). The fluorescence spectrum of the P3HT-PCBM film is shifted to shorter wavelengths compared with the fluorescence spectrum of the P3HT film. Decreasing fluorescence intensity of more than 10 times occurs for the P3HT-KI film compared with fluorescence of P3HT films. Short-wavelength shift of the fluorescence spectrum was observed for the P3HT-KI film similar to shift of the fluorescence spectrum of the P3HT-PCBM film (Figure 1, b, curve 3).

The band gap energy (E_g) of P3HT with organic and inorganic impurities was determined from the absorption spectra of the films (Figure 2). Results of calculation of E_g polymer composites shows in Table 1. These results show that the organic and inorganic impurity is not significantly in changing of the band gap of the composite films.

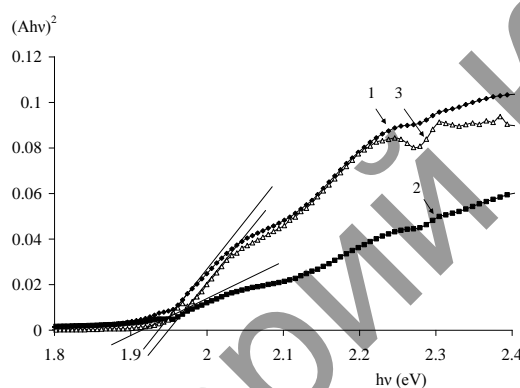


Figure 2. Plot of $(Ahv)^2$ versus $h\nu$ for all the samples along the sequence: 1) P3HT; 2) P3HT - PCBM; 3) P3HT - KI

Figure 3 shows the fluorescence kinetics of P3HT, P3HT-PCBM and P3HT-KI films. Registration signal is at the maximum of the fluorescence spectrum at 650 nm wavelength. Figure 3 shows, that addition of 1% KI in the polymer leads to the same fluorescence quenching as addition of 50% fullerene in P3HT film. The lifetime of fluorescence was calculated from the linear part of the logarithmic curve (Figure 3, b). The results of the fluorescence lifetime measurement are shown in Table 1. The largest decrease in the lifetime of the film was observed for P3HT-KI. Decrease of the lifetime of the compared with decrease P3HT-KI film is observed for the film P3HT-PCBM.

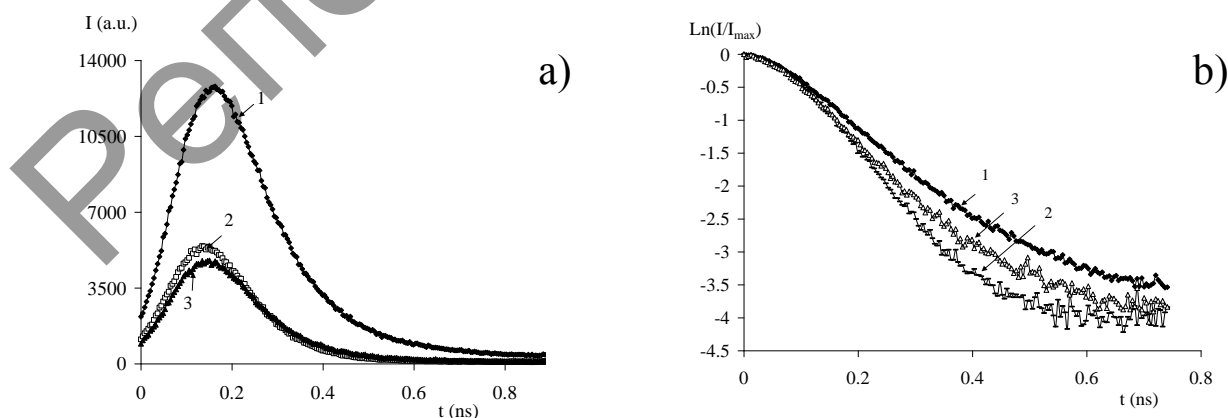


Figure 3. Fluorescence kinetics $I(t)$ (a) and logarithmic curves of fluorescence kinetics (b) for the P3HT film (1), P3HT-PCBM films (2) and P3HT-KI films(3)

Table 1. The size of the band gap, fluorescence lifetime and the lifetime of the free charge carriers in polymer films doped with organic and inorganic impurities

Material of films	Bandgap (eV)	τ_{F1} (ns)	τ_y (s)
P3HT	1,93	0,228	
P3HT-PCBM	1,92	0,184	0,012
P3HT-KI	1,94	0,145	0,012
P3HT-KI (B = 0,55 T)	-	-	0,014

For the P3HT-PCBM film change in fluorescence lifetime associated with the formation of electron-hole pairs at the interface between P3HT and PCBM. For a sample of P3HT-KI quenching of fluorescence due to the dynamic fluorescence quenching through KI. The iodine atom (I) is active not only in quenching of luminescence, but also it increases the probability of intersystem crossing from the singlet (S_1) to the triplet (T_1) state [3].

Solar cells have been made for determination of the free charge carriers lifetime in the polymer films. It was made planar heterojunction P3HT-PCBM instead of bulk heterojunction. KI added to the polymer P3HT. P3HT- KI weight ratio was 100: 1.

Heavy atom can lead to increased intersystem crossing in organic molecules [2]. Dynamic fluorescence quenching film P3HT + KI indicates growth intersystem crossing $S_1 \rightarrow T_1$ in the film of P3HT + KI. An additional factor pointing to the increase of the concentration of molecules in the T_1 state can be a magneto-sensitive processes of transformation of light energy into electrical energy. Figure 4 shows CVC of solar sells with planar heterojunction based on P3HT – PCBM and P3HT+KI – PCBM.

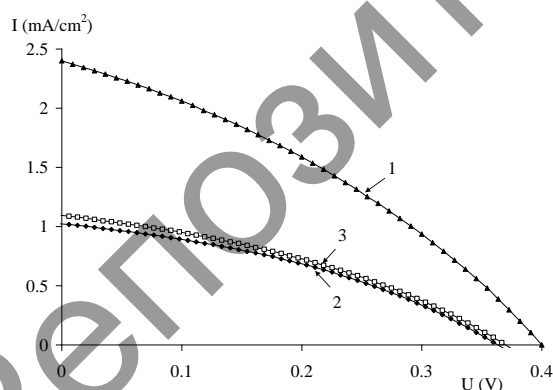


Figure 4. Influence of the external magnetic field on the current-voltage characteristics of solar cells: 1) P3HT- PCBM; 2) P3HT+KI – PCBM (B=0 T); 3) P3HT+KI – PCBM (B=0,55 T)

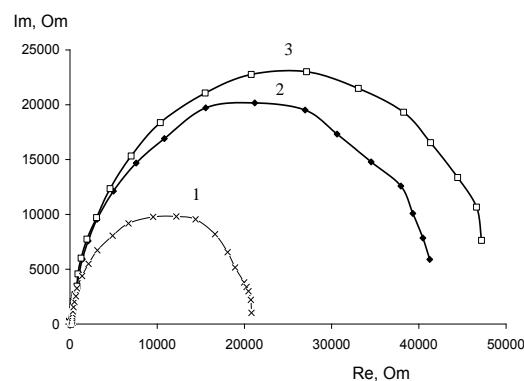


Figure 5. Impedance spectra of solar cells: 1- P3HT- PCBM; 2 - P3HT+KI – PCBM (B=0 T); 3- P3HT+KI – PCBM (B=0,55 T)

Studies of the influence of magnetic field on the CVC of solar cells showed absence of influence of MF on the planar heterojunction of P3HT-PCBM. Analogous results are observed in [6, 7]. It indicate about absence of the formation stage of the polaron pair in the P3HT polymer and effective transformation of excitons into free charge carriers at the interface of the heterojunction. Addition of 1% KI in the film leads to a significant reduction of I_{sc} and a small decrease of the U_{oc} . Influence of an

external magnetic field on the current-voltage characteristics of the solar cells is fixed on the cell containing the impurity of KI. Growth of the U_{oc} and I_{sc} occurs in the magnetic field (Figure 4, curve 3).

Measurement of the electrical impedance of cells shows the effect of an external magnetic field on the electrical resistance of the cells with the addition of KI. The effect of the external magnetic field is not fixed on the cells without KI. The value of both the real part and the imaginary part of the electrical resistance of the P3HT+KI – PCBM cell increases in an external magnetic field (Figure 5). Thus, surprisingly, that the lifetime of the free charge carriers in the magnetic field increases (Table 1).

4. Conclusion

Spectral-luminescent properties of polymer films doped the heavy atom of potassium iodide (KI) have been investigated. Addition of KI in polymer films doesn't lead to significant changes in optical density polymer films and doesn't change the bandgap of the polymer. Fluorescence spectrum of P3HT film have broad band with the maximum at 650 nm and the shoulder at 720 nm. Addition of KI in polymer film leads to decreases of intensity of the fluorescence and change the form of the spectral curve. Investigation of the fluorescence kinetics showed a decrease in fluorescence lifetime in the films of P3HT-PCBM ($\tau_f = 0,184$ ns). This is associated with the formation of electron-hole pairs at the heterojunction interfaces. Quenching of fluorescence intensity and decrease of fluorescence lifetime ($\tau_f = 0,145$ ns) occurs in the film P3HT + KI. It is associated with the dynamic fluorescence quenching polymer P3HT in using KI. The increase in the probability of intersystem crossing from the singlet (S_1) to the triplet (T_1) state is observed in the film P3HT + KI.

Influence of the external magnetic field on the current-voltage characteristics of the solar cells with the addition of a heavy atom indicates an increase intersystem crossing between S_1 and T_1 electronic state of the polymer P3HT. Addition of KI in the amount of 1% leads to a decrease in I_{sc} and slightly decreases U_{oc} . The magnetic field is not affect on the characteristics of photovoltaic P3HT-PCBM solar cell. U_{oc} and I_{sc} is increase in the magnetic field for solar cells with the addition of 1% KI.

Measurement of the electrical impedance of cells shows the same magnetic sensitivity of cells with the addition of KI. The lifetime of the free charge carriers increases in a magnetic field. These results indicate a significant contribution of excited triplet states of the P3HT polymer in the process of transformation of light energy into electrical energy in an organic solar cell

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