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Features of deactivation of excited states of cationic polymethine dye in the matrices of halogen-containing derivatives of poly-N-epoxypropyl carbazole

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ABSTRACT

Singlet and triplet states of the cationic polymethine dye in polymers that are derivatives of poly-N-epoxypropyl carbazole with heavy atoms of different chemical nature were studied. It was shown that the presence of heavy atoms in the structure of the polymer leads to an appearance and rise of the dye phosphorescence due to the growth of the spin-orbit interaction in the dye molecule and increasing in the rate of singlet-triplet transitions. Also, the appearance of recombination luminescence indicated the formation and recombination of electron-hole pairs, which is an additional channel of relaxation of excited states of the dye in hole conducting polymer films. It was shown that external magnetic field leads to decreasing in the intensity of recombination luminescence. The time-dependent behavior of the magnetic effect is the result of competition between the singlet and triplet channels of the formation of the electron-hole pairs.

1. Introduction

Recently, solar cells based on thin organic films are referred as an alternative to inorganic semiconductors solar cells. Despite the potentially high quantum efficiency, there are a number of shortcomings in such solar cells based on thin polymer films, which does not allow starting a large-scale commercial producing these solar cells. The main disadvantage is their low power conversion efficiency (PCE), which usually does not exceed of 6%. However, recently some authors report about improved PCE reaching 11% [1]. Low PCE is mainly the result of low efficiency of generation of free charge carriers followed by small length of the exciton diffusion and not optimized energy levels of donor and acceptor materials.

Singlet excitons are mainly used in organic solar cells. These excitons are formed directly upon light absorption [2]. However, the important role of the triplet state in the process of converting light energy into electrical energy in organic photovoltaic cells was shown in a number of studies [3,4]. In a work [5] higher open-circuit voltage and lower short-circuit current in a device based on 1-(3-(2 ethylamine) hexaoxy carbonyl)propyl-1-phenyl-Lu_3N-C(80) in comparison with the (6,6)-butyric acid methyl ether-phenyl-C(61) was explained by the active formation and migration of triplet excitons in the new substance, which leads to a change in the photovoltaic properties of solar cells.

In the work [6] PCE was increased when $Ir(ppy)_3$ organic molecules, before used in electroluminescent devices, was incorporated. This effect was a result of the participation in the formation of free charge carriers both singlet and triplet excitons. Formation of triplet excitons was associated with an increase in the spin-orbit interaction due to incorporation of $Ir(ppy)_3$ molecules.

Authors of works [3,4] offer to use the process of triplet-triplet annihilation or up-conversion photoluminescence to increase PCE of solar cells and electroluminescent cells. Thus, the study of the role of the triplet state in the process of generation of free charge carriers is important in the problem of improving PCE of organic solar cells.

Dyes are the ones of the active elements involved in the formation and recombination of electron-hole pairs (EHP) in organic solar cells. In this connection, in what spin state the dye molecule will be after photoexcitation becomes important [7–10].

The singlet state of polymethine dyes is well studied and it is a model for carrying out calculations of the electronic states by quantum chemical computation methods. Currently, physicochemical processes with participation of triplet states are interesting to the researchers. Polymethine dyes, containing no heavy atoms in their compositions, have a high quantum yield in the singlet excited state and a small one in the triplet state [7].

However, the population of the triplet state of polymethine dyes can be achieved by increasing of spin-orbit interaction (SOI) in the dye molecule under the influence of an external heavy atom, which is included in the structure of the polymer molecule. It is assumed that heavy atoms in the polymer compound will enhance the SOI in the dye

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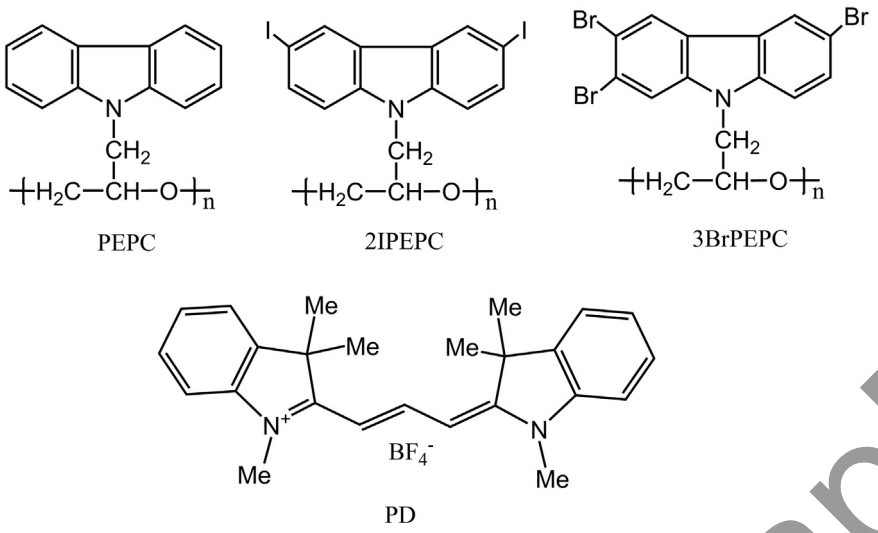

Fig. 1. Structure of dye and polymers.

molecules [11]. This will lead to the growth of the long-lived triplet dye molecules concentration and will increase the probability of electron-hole pair formation in the semiconductor polymer matrix. The use of such composite materials can significantly improve PCE of organic solar cells and LEDs. The role of spin excited states of polymethine dyes in the photoconductivity of dyed photoconductive polymer composites based on polyvinyl butyral (PVB) and poly-N-epoxypropyl carbazole (PEPC) was discussed in [10,12]. It was shown that the addition of a KI impurity to the film of the PEPC + cationic polymethine dye (PD) (Fig. 1) leads to a decrease in the magnetic effect on recombination luminescence (RL) in the millisecond time range [10,12]. Also, a positive magnetic effect was observed for the film PEPC + PD + KI in the initial part of the RL curve.

This work presents the results of study the deactivation of singlet and triplet states of a cationic polymethine dye in polymers – derivatives of poly-N-epoxypropyl carbazole with heavy atoms of different chemical nature.

2. Experimental

Structure formulae of polymers and cationic PD are shown on Fig. 1.

The photonics of this dye and the mechanisms of forming the EHP in the PEPC were investigated and discussed in [10,12].

PEPC and polymer compounds with a different number of heavy atoms – 2IPEPC and 3BrPEPC, were used as polymer matrices. Though the number of heavy atoms in the structure of the monomeric unit is different, it is expected that both polymers will have practically the same effect on intramolecular transitions of different multiplicity in the dye molecule. This follows from the direct dependence of the energy of the spin-orbit interaction (H_{SO}) on the effective charge of the nucleus of a heavy atom (Z_{eff}) [13].

As a non-photoconductive medium, PVB was used. The concentration of the dye in the polymer films was equal to 1% with respect to the weight of the polymer. The dyed polymer films were obtained by drying the dye solution and the corresponding polymer on the glass substrates.

The absorption and fluorescence spectra of the samples were measured on a Cary-300 and Eclipse (Agilent) spectrometers, respectively. Optical cryostat OptistatDN2 (Oxford instruments) was used for measurements of temperature dependence of phosphorescence.

Quantum yields of the fluorescence (φ_{fl}) of the dye in polymer films were measured by the absolute method using the integrating sphere (Avantes) by the method described in [14,15].

Spectral-kinetic measurements of long-lived luminescence were carried out in a vacuum optical cryostat. The photoexcitation of the samples was performed by the second harmonic of the LCS-DTL-374QT neodymium laser. The intensity (I) of the luminescence was registered every other 10 μs after the excitation light was turned off. The signal was accumulated in the form of a number of electrical output pulses coming from the photoelectric multiplier at each time interval. The summation of the output pulses of at least of 500 laser shots was carried out for obtaining a satisfactory signal of the kinetics from the sample.

On the average 1000 output pulses were accumulated. In addition, the decay kinetics of the luminescence of dye films was measured on a pulsed spectrofluorometer with registration in a time-correlated photon counting mode (Becker&Hickl, Germany) in the nanosecond time interval. The lifetime of the luminescence in composite films was determined by using of SPCM Image data collection and analysis software.

Kinetic measurements were carried out both without an external magnetic field and in a magnetic field. To carry out measurements at different temperatures, the sample was placed in a vacuum optical cryostat. The temperature was controlled by a copper-constantan thermocouple. The intensity of the external magnetic field (B) was varied in the range of 0–0.5 T. The magnitude of the magnetic effect was estimated from the relative change in the luminescence intensity in a magnetic field and in the absence of a field by the formula $g(B) = (I_B - I_0)/I_0$, where I_B and I_0 are the intensities of long-lived luminescence in a field and without a field, respectively.

For studying of photoconducting properties of the films, the samples were prepared as the thin polymer film of dye deposited on a transparent conductive layer of SnO_2:In_2O_3 (ITO). The thickness of the films was equal to 1.1–1.2 μm. The measurements were performed according to the following procedure. Initially, the free surface of the film was charged in a corona discharge by positive ions to a potential of 120–130 V relative to the ITO layer. For this purpose, a specially designed device was used in which the corona discharge was formed by applying of constant electric voltage (~ 10 kV) between the ITO layer and the metal filament above the surface of the film. The distance between the free surface of the film and the metal filament was equal to 2 cm. Then, the electric potential (V_p) of the film surface and its changes during irradiation (t_{irr}) with the light from the side of glass substrate with the ITO layer and after switching off the light were measured. The maximum achievable value of the surface potential (V_{pmax}) of the film was determined. Kelvin's method was used for the measurement of V_p and V_{pmax} [16]. An Ag plate with a diameter of 4 mm was used as the sensor of probe. The oscillation frequency of the probe was equal to 80 Hz. The kinetics of the change in V_p upon light irradiation of the composite film was recorded by using of a storage oscilloscope. LED with a maximum radiation intensity at a wavelength

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of λ = 650 nm and a light intensity of 30 cd was used for the samples excitation. The intensity of incident light in the area of sensor was equal to 40 W/m^2. All measurements were taken at room temperature of 20 °C.

For a more detailed characterization of polymers and indicating the role of heavy atoms, quantum-chemical calculations of spectral characteristics were performed by using of TD DFT/B3LYP method (Gaussian 09 W Revision-A.02). The calculation was carried out for the monomeric units of the polymers under study in a vacuum. An estimate of the rates of photophysical processes was carried out by the INDO/s semiempirical method with spectroscopic parameterization, according to [17].

The structure of the investigated polymers was studied by Raman microscope (Confotec MR520 3D Scanning Raman Confocal Microscope) under the excitation by a laser with λ_{gen} = 633 nm.

3. Results and discussion

3.1. Spectral-luminescent and structure parameters of halogen-containing derivatives of poly-N-epoxypropyl carbazole

Spectral and luminescent properties of PEPC and its derivatives were studied. The measured absorption spectra are shown in Fig. 2. As can be seen from the figure, the absorption spectra of the polymers are located as broad bands in the UV region of the spectrum.

There are two bands of almost the same intensity in the absorption spectrum of PEPC. One band is exhibited in the region of 320–360 nm with a maximum of about 340 nm and the second one is from 200 to 300 nm. The edge of the absorption spectrum located at 364 nm. The absorption spectrum coincides with the data given by other authors [18–20]. In the presence of a heavy atom, a bathochromic shift of the long-wavelength absorption band of polymers by almost 20 nm and the manifestation of maxima at 360 and 364 nm was observed. And the absorption band in the region of 200–300 nm remains practically unchanged.

Calculations of the electronic structure and photophysical processes in the molecules of PEPC, 2IPEPC and 3BrPEPC were performed for monomer units. The calculated positions of the energy levels and the oscillator strengths of PEPC molecule are shown in the Table 1. In particular, an absorption spectrum with maxima at 249, 290 and 336 nm was obtained. The oscillator strengths were equal to 0.45, 0.3 and 0.05, respectively.

As can be seen from the data, an optically allowed transition at 336 nm for the PEPC, as well as slightly allowed transitions of about 360 nm for 2IPEPC and 3BrPEPC, is mainly formed by redistribution of

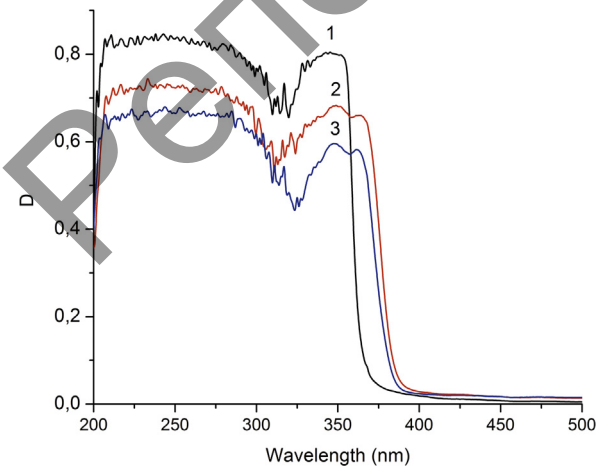

Fig. 2. Measured absorption spectrum of films of: 1 – PEPC; 2 –2IPEPC; 3 – 3BrPEPC.

Table 1
Calculated spectral parameters of monomeric unit of PEPC and its derivatives.

State	*E*, eV	λ, nm	*f*	Occupied molecular orbital	Unoccupied molecular orbital	% of contribution
PEPC						
S_1	3.6886	336	0.05	HOMO	LUMO	69
				HOMO-1	LUMO + 1	14
S_2	4.2739	290	0.30	HOMO	LUMO	63
				HOMO-1	LUMO + 1	20
				HOMO-1	LUMO	11
S_3	4.9778	249	0.45	HOMO	LUMO + 1	57
				HOMO-1	LUMO	26
				HOMO	LUMO + 2	16
S_4	5.1023	243	0.06	HOMO-1	LUMO	17
				HOMO-2	LUMO	62
				HOMO-1	LUMO + 2	18
S_5	5.1425	241	0.2	HOMO-1	LUMO + 1	57
				HOMO	LUMO + 2	36
S_6	5.5936	221	0.12	HOMO	LUMO + 2	53
				HOMO-3	LUMO	31
S_7	5.6936	218	0.51	HOMO	LUMO + 3	60
				HOMO	LUMO + 1	19
				HOMO-1	LUMO	18
S_8	5.9438	209	0.11	HOMO-2	LUMO	44
				HOMO	LUMO + 3	41
				HOMO-1	LUMO + 2	15
2IPEPC						
S_1	3.4364	361	0.025	HOMO	LUMO	69
				HOMO-1	LUMO + 3	10
S_2	4.0127	309	0.08	HOMO-1	LUMO	64
				HOMO	LUMO + 3	25
				HOMO-2	LUMO	12
S_3	4.4820	276	0.11	HOMO	LUMO + 2	51
				HOMO-2	LUMO	45
S_4	4.7228	262	0.001	HOMO-1	LUMO + 2	65
				HOMO	LUMO + 1	17
S_5	4.7780	259	0.74	HOMO-2	LUMO	51
				HOMO	LUMO + 3	38
3BrPEPC						
S_1	3.4072	364	0.03	HOMO	LUMO	70
				HOMO-1	LUMO + 2	12
S_2	3.9947	310	0.007	HOMO-1	LUMO	62
				HOMO	LUMO + 3	28
S_3	4.5800	271	0.16	HOMO-2	LUMO	68
				HOMO-1	LUMO	12
S_4	4.6015	269	0.35	HOMO	LUMO + 3	55
				HOMO-3	LUMO + 2	33
S_5	4.7169	262	0.40	HOMO-3	LUMO + 2	57
				HOMO-1	LUMO + 2	27

the electron density between HOMO-LUMO orbitals with some admixture of neighboring orbitals. It can be concluded that a heavy atom in the structure of the polymer molecule leads to a bathochromic shift of the absorption spectrum. This is a consequence of the lowering of the excitation energy due to the shift in the distribution of the electron density in the π-electron system of the 2IPEPC and 3BrPEPC chromophores. Meanwhile the short-wave absorption band for all polymers at 200–300 nm is formed mainly by a transition between the ground and highly excited states of S_3 and above, in the formation of which, mainly, the transitions between the high-energy molecular orbitals HOMO-1, HOMO and LUMO + 1, LUMO + 2 etc. are included. The absorption band in the region of 320–360 nm is associated with transitions between the states of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$.

The emission spectra, registered upon excitation of films based on PEPC, 2IPEPC and 3BrPEPC with λ = 340 nm are shown in the Fig. 3.

As can be seen from the figure, several peaks were observed in the fluorescence spectrum of the PEPC. At room temperature, the main maximum was located at 426 nm with a shoulder of about 380 and 364 nm. Lowering in the temperature leads to an increase in the intensity of the luminescence of the polymer at 364 and 380 nm, and also to a decrease of intensity at 426 nm. The last band manifests as a

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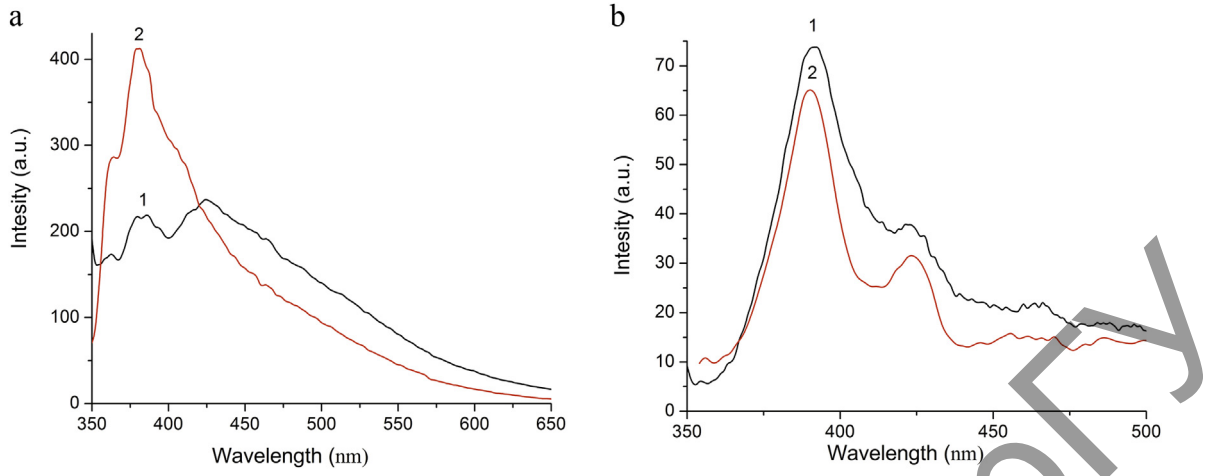

Fig. 3. Fluorescence spectrum of film based on (a) PEPC (λ_{ex} = 340 nm) at temperature of: 1 – 293 K, 2 – 77 K; (b) 1 – 3BrPEPC and 2 – 2IPEPC at T = 293 K.

shoulder on the fluorescence curve. Analyzing the obtained data, it can be say that the emission with a maximum at 360 and 380 nm is the emission of monomeric centers. While the long-wavelength emission band at about 420 nm is associated with the formation of excimers [21]. Lowering in the temperature of the film leads to a decrease in the efficiency of their formation, which is a known phenomenon [22]. As a result, the intensity of the monomeric luminescence increases.

For the polymers with heavy atoms the bathochromic shift of fluorescence band was registered (Fig. 3b). Meanwhile the changes in the relation of intensity of monomeric and excimer centers was observed. Thus, a maximum at 390 nm becomes more intense, and a luminescence of about 422 nm manifested as shoulder of a spectrum curve. At the same time, the fluorescence intensity of the 3BrPEPC and 2IPEPC films is almost in 3 times less than the intensity of the emission of PEPC. The fluorescence lifetimes recorded at 420 nm were equal to 4 ns for the PEPC, 1.1 ns for the 2IPEPC and 1.6 ns for the 3BrPEPC.

As can be seen from the data obtained, the luminescence spectrum of the polymer does not almost overlap with the luminescence spectrum of the chosen dye. And when the pure polymer were excited with a laser with λ_{gen} = 532 nm, emission of film was not recorded.

The effect of a heavy atom on the photophysical intramolecular processes in the monomer molecule was studied. For this purpose, the rate constants of the radiative process (k_r, solid lines), internal conversion (k_{vc}, wavy lines) and intercombination conversion (k_{ic}, dotted lines) were estimated. For the PEPC molecule, the scheme shown in Fig. 4 was obtained.

It is seen from the figure that the molecule, absorbing the light with λ = 340 nm, passes into the S_1 state. Further, it can either transit to the S_0 state, or to the nearby T_2 and T_3 triplet states. Then, a emission of phosphorescence is possible after the nonradiative relaxation to the T_1 level. The addition of a heavy atom to the polymer structure leads to a decrease in the energy of the triplet states of the monomer (Fig. 5). This also increases the probability of intercombination transitions from the S_1 state and the probability of the radiative decay of the T_1 state. This means that the existence of phosphorescence is very likely for the investigated polymers. For the 2IPEPC molecule, the calculated position of the triplet levels were slightly shifted to the red region (about 5 nm), and the transition rates was the same order of magnitude as for the 3BrPEPC.

The phosphorescence spectra of polymer films were measured when they were excited by light with λ = 340 nm. The phosphorescence spectrum of PEPC was registered as a broad band with a maximum at 490 nm, which shifts to the long-wavelength region for macromolecules with heavy atoms. The maximum of the phosphorescence spectrum of the 3BrPEPC was located at 550 nm, while for the 2IPEPC this parameter was equal to 590 nm. The registered phosphorescence maxima are close in energy value with the calculated position of the T_1 state. When the temperature of the films was lowered to 77 K, an increase in the intensity of phosphorescence was observed without changing in the position of the luminescence band. The lifetimes calculated from the long-term part of decay kinetics are shown in Table 2.

It is seen, that the presence of a heavy atom leads to a decrease in the lifetime of phosphorescence. τ_{phos} decreases in the range of PEPC-3BrPEPC-2IPEPC.Thus, it was shown that in halogen-containing PEPC the probability of intercombination conversion is higher, which leads to a markedly more intense phosphorescence and reducing its lifetime. Similar effects were obtained for the colored films of the polymers under study.

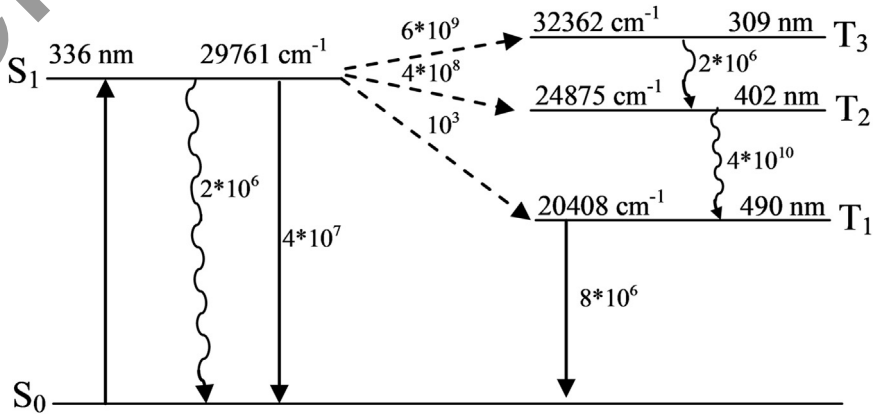

Fig. 4. The scheme of electron states and intramolecular transitions in the monomer unit of PEPC. The rate constants are in s^{-1}.

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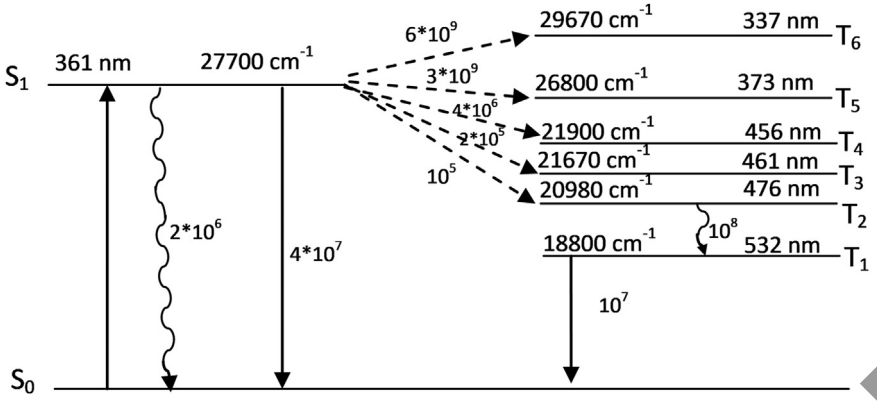

Fig. 5. The scheme of electron states and intramolecular transitions in the monomer unit of 3BrPEPC. The rate constants are in s^{-1}.

Table 2
Lifetimes of phosphorescence of polymer films, T = 77 K.

Sample	λ_{reg}, nm	τ, ms
2IPEPC	590	5
3BrPEPC	555	5
PEPC	505	9

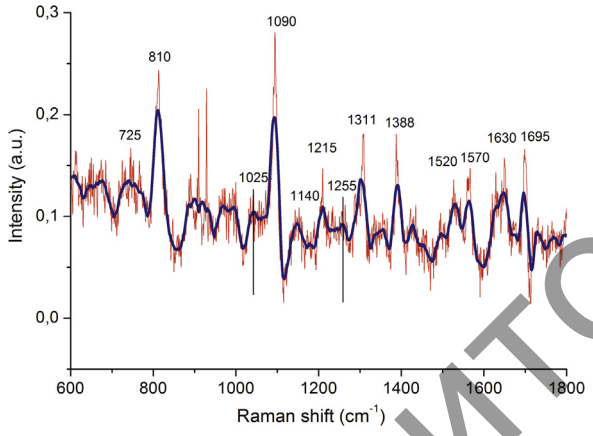

Fig. 6. Raman spectra of PEPC film.

The Raman spectrum of PEPC was registered (Fig. 6). There are following groups of the lines can be assigned [23,24]: at 725, 1025, 1255, 1311 and 1690 cm^{-1}, associated with the vibration, rotation and stretching of the bonds of polyvinyl part. Bands at 1495 and 152 cm^{-1} are the result of the stretching of the bond in the 5-membered hetero-ring and vibration of the C–H bonds in it. The remaining peaks in the region of ~ 1115–1550 cm^{-1} nm belong to the changes occurring in the benzene rings – the deformation of the C–H bonds, the stretching of the C=C and C–C bonds. It can be noted that the band of about 1255 cm^{-1} is associated with the vibration of the epoxy bond of the PEPC molecule.

Similar spectra were obtained for 2IPEPC and 3BrPEPC. Additional band of about 1595–1600 cm^{-1} was recorded in mentioned polymers, which can be associated with substituted benzene derivatives in the carbazole part of the monomer [25].

3.2. Deactivation of excited states of cationic polymethine dye in polymer photoconductive matrix

As was shown in [12] the absorption and fluorescence spectra of PD dye in ethanol solution are presented as intensively bands with the maxima at 540 nm for absorption and 570 nm for fluorescence. The blue-shifted additional peak was recorded on the absorption spectrum.

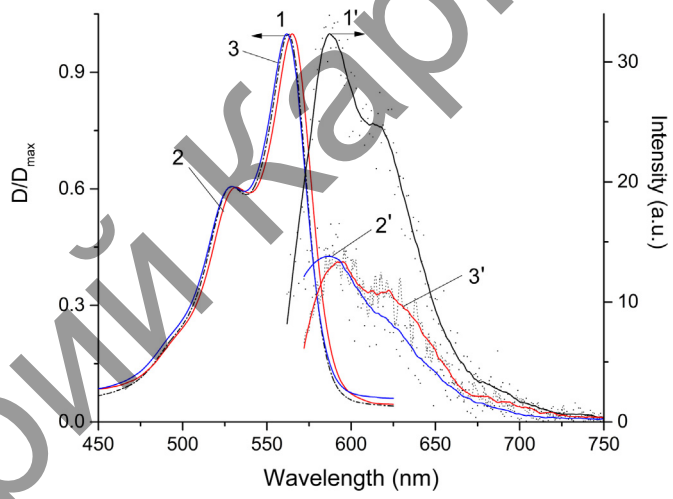

Fig. 7. Absorption (1 − 3) and fluorescence (λ_{ex} = 550 nm, 1' – 3') spectra of PD dye in polymers: 1, 1' – PEPC; 2, 2' – 2IPEPC; 3, 3' – 3BrPEPC.

For fluorescence, a peak shifted to the long-wavelength region was also observed. The measured spectra of absorption and fluorescence of the dye in polymer films are shown in Fig. 7.

It is seen from the figure that the maximum of the absorption spectrum of the PD dye in the PEPC exhibits at 560 nm with a short-wavelength shoulder of about 530 nm. The fluorescence band exhibits a maximum at 587 nm with a shoulder at 617 nm. In polymer films with a heavy atom, a slight bathochromic shift of the absorption and fluorescence bands was registered (Table 3). At the same time, the intensity of the dye fluorescence in 2IPEPC and 3BrPEPC films is almost in two times less than the emission intensity in the PEPC. Results of measurements of the quantum yield of fluorescence of dye in polymer films was showed (Table 3) that φ_{fl} of the dye decreased almost in 2-fold in the films of 2IPEPC and 3BrPEPC as compared with PEPC, which is correlates with a decrease in the fluorescence intensity. The observed

Table 3
Spectral parameters of PD dye in polymer films.

Polymer	PEPC	2IPEPC	3BrPEPC
[a] $\lambda_{1\ max}$, nm	561	565	562
[a] $\lambda_{2\ max}$, nm	528	530	528
$\Delta\lambda^{a}_{1/2}$, nm	57	58	58
[f] $\lambda_{\ max}$, nm	587	590	590
[f] $\lambda^{sh}_{\ max}$, nm	617	617	617
$\Delta\lambda^{f}_{1/2}$, nm	66	68	68
τ, ns	1.3	1.5	1.4
φ_{fl}	0.05	0.02	0.02

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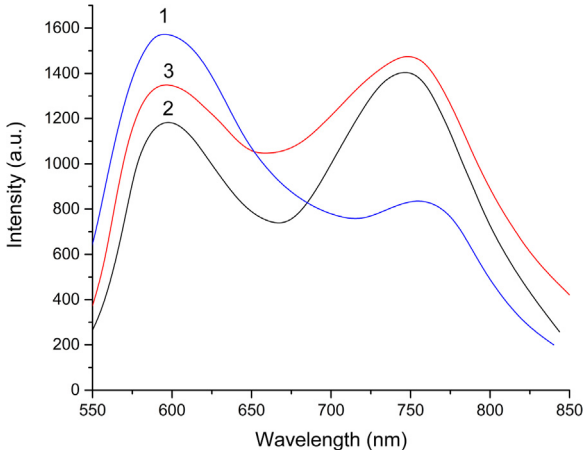

Fig. 8. Long-lived luminescence of PD dye in polymer: 1 – PEPC; 2 – 2IPEPC; 3 – 3BrPEPC. T = 100 K.

quenching both in intensity and in quantum yield is the result of the enhancement of the interconversion into the triplet state of the dye. This is connected with increasing in SOI in polymer composite with heavy atoms [11,26]. The fluorescence lifetimes of the dye practically do not depend on the type of polymer and are equal to 1.4 ± 0.2 ns, both for PEPC, 2IPEPC, 3BrPEPC, and for PVB.

Long-lived dye luminescence of PD + PEPC was registered temperature of T = 100 K. The recorded spectra consist of two bands. The short-wave band with a maximum at about 590 nm coincides spectrally with the fluorescence spectrum under steady-state photoexcitation (Fig. 8) and is due to the radiative transition from the singlet-excited state S_1 to the ground state S_0 [10,12]. Also in the long-lived luminescence spectrum a broad band exhibits in the region of 700–850 nm with a maximum of about 750 nm, which is a phosphorescence band (PHOS) of the dye.

To confirm the nature of this luminescence the temperature-dependent emission spectra of PD in polymer matrix were measured. The temperature of the sample was varied from 77 to 280 K. The measurements were carried out on spectrophotometer Eclipse (Agilent). Obtained spectra are shown in the Fig. 9.

Measurements have shown that increasing in the temperature does not change the shape and position of the luminescence spectra, and the PHOS intensity of the dye in polymer films decreases. The intensity versus temperature curves for all three polymer matrices have a similar shape (inset of Fig. 9) and can be described by an exponential function.

The intensity of PHOS undergoes to intense quenching, mainly in the temperature range from 100 K to 200 K, after that the intensity changes a little. The greatest intensity quenching, which was estimated from the difference of $I_{100\,K}$-$I_{300\,K}$, was obtained for films of PD in 3BrPEPC, then for 2IPEPC and PEPC samples.

The measurements of the decay luminescence kinetics at the λ_{max} = 590 nm, have shown that the emission decays more slowly in the PEPC matrix than in the PVB (Fig. 10). The lifetime, calculated from the long-term part of the decay kinetic curve, is equal to 0.5 ms for a PD in PVB, which is shorter than the lifetime of the dye luminescence in PEPC films (Table 4). As was shown in [12], the observed difference in the luminescence duration of PD in these polymers is result of presence of a portion of the RL in the total luminescence along with the delayed fluorescence (DF) $S_1 \rightarrow S_0$. The nature of DF is associated with the interconversion of dye molecules from T_1 state to the S_1 state [10,12]. A slower RL is associated with the formation of the EHP of the cation-radical of the carbazole fragment of PEPC and the electro-neutral radical of the PD.

Thus, the following processes are developed as a result of photoexcitation of PD in the matrix of PEPC:

$S_1 \rightarrow S_0 + h\nu_{fl}$ (fluorescence)
$S_1 \rightarrow T_1 \rightarrow S_0 + h\nu_{ph}$ (phosphorescence)
$T_1 \rightarrow S_1 \rightarrow S_0 + h\nu_{dfl}$ (delayed fluorescence)
T_1(dye) + S_0(PEPC) $\rightarrow$ [T_1^-(dye) S_0^+(PEPC)] $\rightarrow$ S_0 (PEPC) + $T_1 \rightarrow$ S_1(dye) $\rightarrow S_0 + h\nu_{rl}$ (recombination luminescence).

As can be seen from the data in Table 4, the lifetimes of long-lived luminescence and PHOS are practically equal in the 3BrPEPC polymer, which allows us to conclude that the long-lived luminescence of the dye in 3BrPEPC is predominantly associated with the intercombination transition from the T_1 to S_1 state and the subsequent emission of a light quantum. The portion of RL in the intensity of integral long-lived luminescence decreases in the series of polymers: PEPC, 2IPEPC and 3BrPEPC.

The conclusion about a decrease of portion of the recombination component in the integrated intensity of the DF of films can be more accurately established under the studying the effect of an external magnetic field on the luminescence intensity. Since the external magnetic field is not have the effect on the intensity of the thermally activated DF from T_1 to the state S_1 [26–29], an increase or decrease in the magnitude of the magnetic effect on the intensity of long-lived luminescence of PD will make it possible to determine the nature of the effect of the heavy atom on RL.

The study of RL of dye in polymers films with various heavy atoms at the boiling point of liquid nitrogen were carried out to establish the role of the triplet state in the formation and recombination of the EHP of PD dye. Lowering in the temperature slows the process of EHP recombination to the temporary resolution of the used luminescence

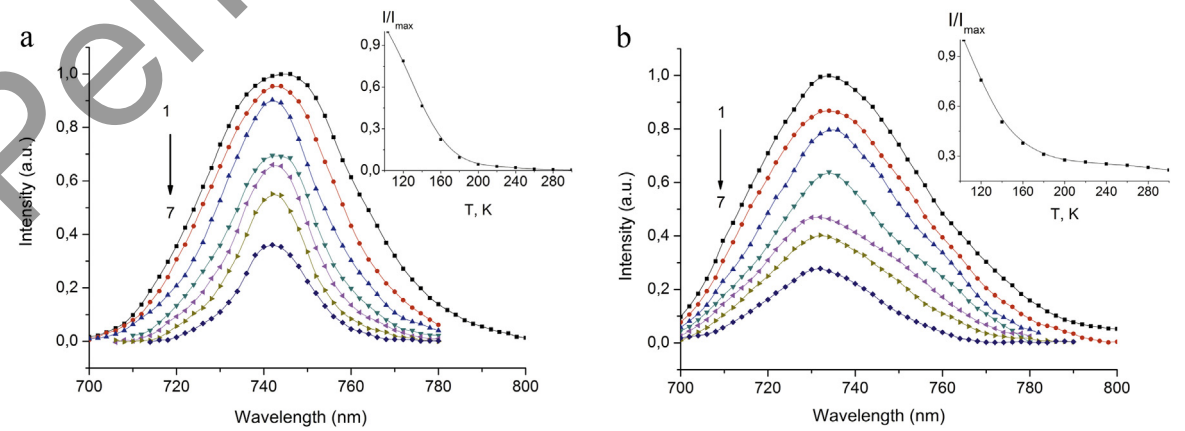

Fig. 9. Phosphorescence spectra of PD in the polymer films of PEPC (a) and 3BrPEPC (b) at temperature of, K: 1 – 77; 2 – 100; 3 – 135; 4 – 160; 5 – 190; 6 – 220; 7 – 250.

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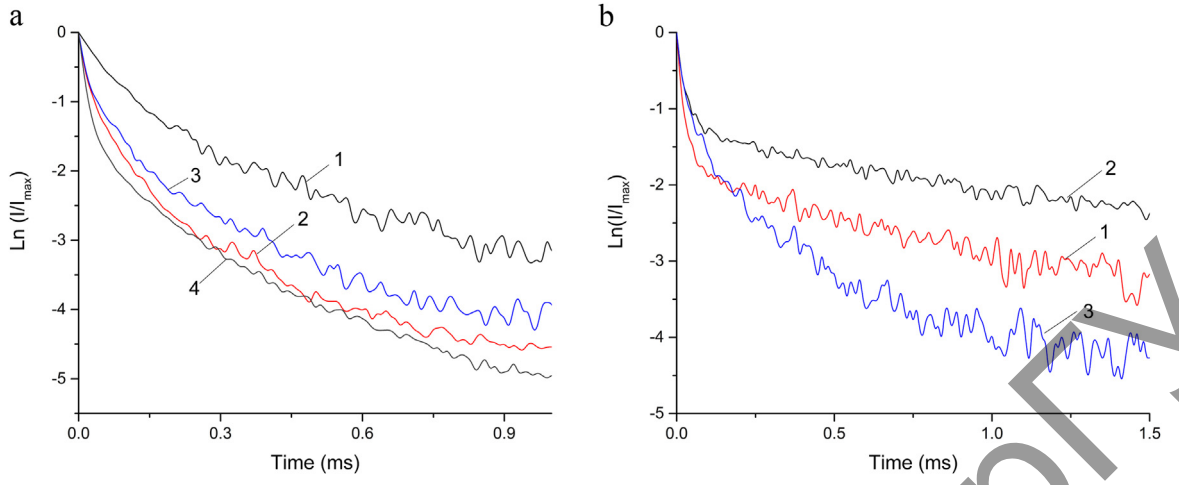

Fig. 10. Decay kinetics of (a) long-lived luminescence (λ_{reg} = 590 nm) and (b) phosphorescence (λ_{reg} = 750 nm) of PD in films of: 1 – PEPC; 2 – 2IPEPC; 3 – 3BrPEPC, 4 – PVB. T = 80 K.

Table 4
Maxima of spectra and lifetimes of long-lived luminescence of PD in polymer films.

Polymer	PVB	PEPC	2IPEPC	3BrPEPC
$^{f}\lambda_{max}$, nm	585	587	590	587
$^{DF}\lambda_{max}$, nm	590	593	593	593
τ_{lum}, ms	0.5	1.0	0.8	0.7
$^{PHOS}\lambda_{max}$, nm	755	750	750	750
τ_{PHOS}, ms	–	1.2	0.9	0.8
I_{lum}/I_{PHOS}	–	1.84	0.84	0.90

recording system. In addition, according to [11], a decrease in temperature should attenuate the contribution of the thermally activated DF to the total intensity of the luminescence.

The dependence of the magnetic effect is shown in Fig. 11a. The value of *g(B)* falls in the series of PEPK – 2IPEPC –3BrPEPC – PEPC + KI films (Fig. 11). For the dye in PEPC matrix, a negative magnetic effect was observed, and $g = 26\%$ for $B \sim 0.5$ T. In the matrices of 2IPEPC and 3BrPEPC, the effect of the magnetic field is smaller. The value of *g* decreases from 10% to 6% at a value of $B \sim 0.5$ T with increasing in number of heavy atoms in the polymer unit. In the PEPC film with the addition of an external heavy atom (salt KI), the magnitude of the magnetic effect was equal to 5%.

Also, in the time range after 0.2 ms value of *g(B)* decreases with a further increase in time for the polymer films of 2IPEPC and 3BrPEPC (Fig. 11b, curves 2 and 3). For the PEPC + KI film, the decrease in *g(B)* occurs in a another time range – starting from 0.6 ms. The value of *g(B)* becomes close to 0 at $t_{reg} \sim 1.2$ ms. Decrease in *g(B)* was not registered in the accessible time range for PEPC film with polymethine dye.

It is well known that the singlet-triplet (S-T) conversion of EHP is the magnetosensitive stage [28,29]. A decrease in the intensity of RL in a magnetic field shows that the formation of EHP mainly proceeds along the triplet channel ($S_1 \rightarrow T_1 \rightarrow T_{EHP}$). The magnetic field reduces the probability of annihilation of triplet EHPs and increases the probability of their dissociation into free charge carriers. EHP pair was formed by the cation-radical fragment of PEPC and the electro-neutral radical of PD. The charge carrier (electron), that is located on the dye molecule, was in a stationary state, while the hole can move along the polymer chain of PEPC. When the Coulomb barrier is overcome by a hole, the bound EHP can form free charge carriers. In the opposite case, there will be a recombination of charge carriers with subsequent emission of a light quantum. As shown by measurements of the time dependence of the magnetic effect (Fig. 11b), the presence of a heavy atom in the polymer leads to a decrease in the lifetime of triplet EHP. In the case of the presence of an external heavy atom (PEPC + KI), the lifetime of triplet EHPs is greater than in the films of 2IPEPC and 3BrPEPC. Thus, the processes occurring in the polymer chain play a decisive role in the EHP lifetime.

The decrease in *g(B)* with the addition of a heavy atom to the sample is due to the competing effect of SOI and external magnetic fields on spin-selective processes involving the excited triplet states of dye molecules. A heavy atom leads to an increase in the concentration of triplets in the sample and increases the probability of both transitions

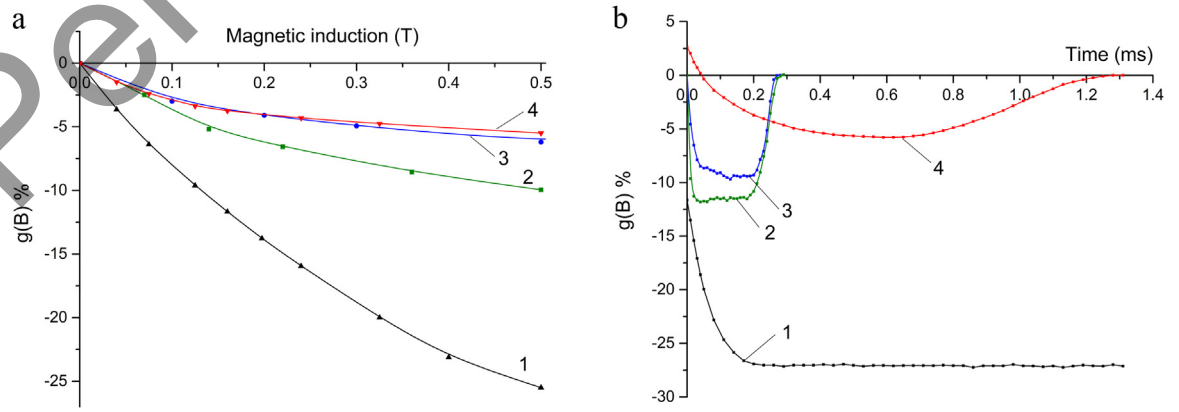

Fig. 11. (a) Magnetic field effect on long-lived luminescence (λ_{reg} = 590 nm) and (b) time dependence of magnetic effect of PD in films of: 1 – PEPC; 2 – 2IPEPC; 3 – 3BrPEPC; 4 – PEPC + KI.

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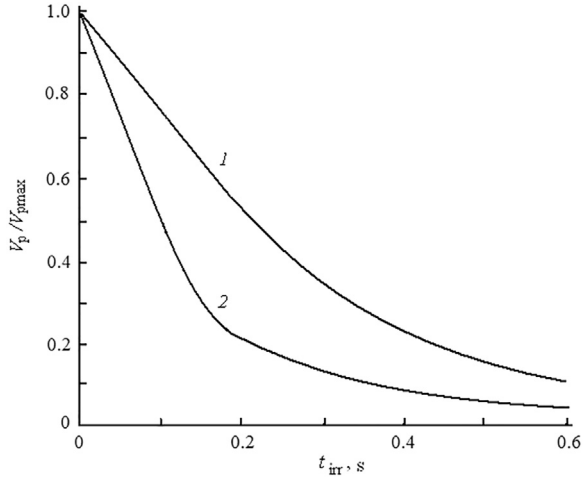

Fig. 12. Normalized curves of decay kinetics of electric potential of PD + PEPC (1) and PD + 3BrPEPC (2) films after their charging in the corona discharge and the beginning of irradiation with light.

from the singlet state to the triplet state and vice versa. This in turn reduces the degree of influence of the external magnetic field on the transitions of the EHP from one spin state to another. At times above 200 μs, a reduction in the concentration of the EHP and a decrease in the contribution of recombination luminescence to the intensity of total luminescence may occur.

To confirm the growth of the concentration of triplet EHPs as a result of singlet-triplet conversion induced by heavy atoms, additional studies of the photoconducting properties of PD dye in PEPC matrices without a heavy atom and with it were carried out.

Normalized curves of decay kinetics of electric potential of PD + PEPC and PD + 3BrPEPC films after their charging in the corona discharge and upon irradiation with light are shown in Fig. 12.

As can be seen from the figure, the rate of decrease in the surface potential of the film is smaller for samples with 3BrPEPC compared with PEPC. This speed can be estimated by the time interval ($t_{0.5}$), for which the value of V_{pmax} was decreased by a factor of 2. For the PEPC based films, the value of $t_{0.5}$ is equal to 0.22 ± 0.02 s, and for the films of PD + 3BrPEPC – 0.10 ± 0.01 s. The latter means that in the films of PD + 3BrPPEK the rate of surface discharge under the light is greater than in similar films based on PEPC.

The increase in the discharge rate of surface of dye films based on 3BrPEPC can be associated with three reasons: 1) an increase in the concentration of mobile nonequilibrium charge carriers due to the increase in the quantum yield of their photogeneration (formation); 2) an increase in the mobility of nonequilibrium charge carriers; 3) an increase in the concentration of long-lived (triplet) EHP as a result of the S-T-conversion of EHP.

The first reason can be associated with an increase in the energy difference of the upper filled orbitals (HOMO) of the dye molecule and donor fragments of the polymer [30]. It means that the energy barrier for geminal recombination of holes also increases. However, this energy barrier for carbazolyl fragments and dye molecules is equal to several tenths of eV [2]. The introduction of bromine atoms into the carbazolyl fragment of 3BrPEPC was accompanied by a bathochromic shift of the absorption spectrum in comparison with PEPC (Fig. 2). The energy difference of the long-wave maximum, which is proportional to the HOMO energy, is equal to 0.2 eV. The latter means that the energy of the energy of potential barrier for holes recombination should decrease on 0.2 eV and, as a consequence, the lifetime of the photogenerated charge pairs and the quantum yield of photogeneration of nonequilibrium charge carriers should be decreased also. But the latter contradicts to the obtained experimental data (Fig. 12).

The second reason can be associated with a decrease in the average distance between the donor fragments of 3BrPEPC, through which occurs the transport of nonequilibrium holes, or/and by the effect of halogen atoms on their mobility. The latter was not the aim of this work and it is the subject of our further research.

The third reason is most significant in our opinion, since the part of recombination luminescence was decreased in the films of PD + 3BrPEPC with the comparison with PD + PEPC.

4. Conclusions

Thus, in polymer matrices with heavy atoms quenching both fluorescence and long-lived luminescence in short-wave range was observed At the same time, bathochromic shift of the absorption and fluorescence spectra of the dyes occurs by almost 15 – 20 nm in the polymeric matrices in comparison with the solutions, however, no deformation of the absorption and fluorescence bands were recorded. The half-width of the spectra remains also constant. The observed spectral shifts can be related to the nucleophilic solvation of ions of dyes and polar groups of polymers [8]. The presence of heavy atoms in the structure of the polymer leads to the appearance and rise of phosphorescence of dye due to the growth of spin-orbit coupling in the dye molecule and an increase in the rate of singlet-triplet transitions in the presence of a polymer with a larger number of heavy atoms.

In polymeric films with a hole conductivity and with a cationic polymethine dye, an additional channel for the relaxation of excited states is the formation and recombination of the EHP that manifests itself in the appearance of RL, which contribute to the total luminescence intensity. In the external magnetic field, the intensity of the RL decreases. The magnetic effect has a time-dependent character due to the competition between the singlet and triplet channels of the EHP formation. The measurements have shown that decreasing of life times of triplet EHPs is greater in the presence of the heavy atom in the structure of halogen-containing derivatives of PEPC, than in the presence of external heavy atom in the PEPC matrix.

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