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Features of photoluminescence of oxygen-saturated films of methoxypolyphenylene vinylene (MEH-PPV)

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The effects of the influence of the magnetic field on the luminescence intensity of methoxypolyphenylene vinylene (MEH-PPV) films at various air pressures above the samples are investigated. An inversion of the sign of the magnetic field effect was detected with a smooth change in the oxygen concentration in the system. Based on the balance equations, a theoretical model of processes is proposed that takes into account the formation of populations of triplet (T) excitons of MEH-PPV and singlet oxygen during the reactions of triplet-triplet annihilation, T-${}^3\Sigma_g(\mathrm{O}_2)$-quenching and T-${}^1\Delta_g(\mathrm{O}_2)$-cross-annihilation of electronic excitations. According to the proposed theoretical model, the magnetic field effects of delayed fluorescence at different concentrations of O_2 molecules in MEH-PPV films are calculated, consistent with the experimental results.

Keywords: triplet excitons, π-conjugated polymers, magnetically dependent fluorescence, singlet oxygen.

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Introduction

Conjugated polymers are a kind of macromolecular system, the structural features of which largely determine its electrical and optical properties. Such polymers are essentially quasi-one-dimensional molecular solids and for this reason are most commonly associated with organic semiconductors. Typical representatives of this group are poly(para-phenylene vinylene) (PPV) and its substituted derivatives such as poly[2-methoxy,5-(2′-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV), interest in which is due to the high efficiency of their electroluminescence, as well as great technological prospects. Conjugated polymers are proposed to be used as an emitting layer for displays, in electroluminescent devices with improved characteristics, and in light indicators.

At the same time, it is necessary to take into account that the photooxidation of these polymers, which always takes place, leads to the formation of defects that act as exciton dissociation areas, which, in turn, leads to photoluminescence quenching [1] and an increase in photoconductivity. Thus, while, on the one hand, photooxidation of MEH-PPV leads to deterioration in the characteristics of electroluminescent devices based on conjugated polymers, on the other hand, their controlled photooxidation can provide an increase in the output parameters of photoelectronic cells and modules with integrated photocells. For this reason, study of photooxidation processes in conjugated polymer systems is of considerable interest for optimizing the properties of materials and improving the characteristics of devices based on such polymers.

When irradiated with light, a part of the excited luminophore molecules transforms into a metastable triplet state (T). This state is quenched by oxygen in its ground, unexcited state ${}^3\Sigma_g$. In many cases, the photooxidation process with PPV derivatives begins with the formation of singlet oxygen ${}^1\Delta_g(\mathrm{O}_2)$ by transferring energy from long-lived T-excitons according to the scheme [1]

$$T + {}^3\Sigma_g^-(\mathrm{O}_2) \to S_0 + {}^1\Delta_g(\mathrm{O}_2), \qquad (1)$$

where S_0 — ground state of luminophore. Thus, generation, dynamics, and decay of triplet excitons, as well as singlet excitations ${}^1\Delta_g(\mathrm{O}_2)$, play an extremely important role in the photooxidation process. In the article [2], the authors used two-photon photoemission to study the dynamics of long-lived T-excitons both in the original, not subject to photoreactions, and in photooxidized MEH-PPV films. To explain the observed dependence of the total photoelectron yield, they used a mathematical model based on rate equations for density of T-excitons. In case of initial film samples not subjected to photooxidation, it was found that exciton triplet-triplet annihilation (TTA) is a rather effective decay channel for T-excitations in MEH-PPV. During photooxidation, the energy level of the T-exciton decreased, and the width of the T-exciton photoemission spectral line decreased significantly. The authors explained both observed effects by modification of the molecular and electronic structure of the films resulting from formation of carbonyl defects in the polymer chains. In addition, they, like many other authors, also observed a typical decrease in the T-exciton lifetime associated with highly efficient quenching of T-excitations by molecular oxygen.

In recent years, there has been an increase in interest in studying the magnetic field effect in processes typical of organic LEDs, such as magnetically sensitive conduction and magnetic electroluminescence luminescence. In the article [3], the authors demonstrated the presence of the magnetic field effect in spectroscopy of the excited state of films of the prototype of π-conjugated polymer — soluble derivative of poly(phenylene vinylene)[2-methoxy-5-(2_-ethylhexyloxy)-poly(p-phenylene vinylene)]−MEH-PPV. Influence of the field manifested itself in magnetic photoinduced absorption (MPA) and also in magnetic photoluminescence (MPL) of polymer samples. The authors studied these magnetic field effects in unmodified MEH-PPV films as well as in MEH-PPV films subjected to prolonged illumination. In addition, mixtures of MEH-PPV with a fullerene derivative were used as objects of study. The MPA and MPL effects arise due to magnetic interactions leading to spin mixing of the pair states of the reagents. These include hyperfine interaction in polaron pairs, zero field splitting (ZFS) in T-excitons, and Zeeman interaction. Thus, manifestations of the ultra-low magnetic field effect at magnetic induction of $B < 0.5$ mT in organic diodes are also observed in MPA of MEH-PPV films with polaron excitations, thus identifying hyperfine interaction as the main mechanism of magnetosensitivity, which leads to mixing of spin states in polaron pairs.

The active influence of molecular oxygen on the long-lived luminescence of organic substances and its sensitivity to magnetic field is usually associated either with O_2 paramagnetism or with its specific electronic structure [1]. Much attention has been paid to a detailed study of magnetic effects in oxygen-containing systems, since they provide unique information about the nature of intra- and intermolecular interactions and the kinematics of reacting particles. In [4,5], oxygen quenching of T-states of luminophores was subject to testing for magnetosensitivity. The spin selective selection criteria for this process are the same as for TTA. For this reason, it could be expected that the response of the system to an external magnetic action would also be similar. However, the authors [5] found that in fields with induction up to 14.5 T, there is no magnetic effect in the liquid oxygen-containing solutions studied by them. In their article, they pointed out a direct connection between the nature and magnitude of the magnetic effect, on the one hand, and the energy structure of the molecular T-$\Sigma_g^-(O_2)$-complex, on the other hand. Kearns and Stone [4] estimated the exchange splitting in the T-$\Sigma_g^-(O_2)$-pair to be $10\,\mathrm{cm}^{-1}$ and expected the manifestation of influence of the field at induction values up to 5 T. Based on the fact that there is no magnetic effect in the T-$\Sigma_g^-(O_2)$-quenching reaction in [5] it was concluded that there is a large exchange splitting in the bimolecular T-$\Sigma_g^-(O_2)$-complex ($\sim 30\,\mathrm{cm}^{-1}$), which significantly exceeds the values of the ZFS parameters of each of the reagents.

In [6], O_2-quenching of T-states of anthracene and pyrene in liquids was indicated by annihilation delayed fluorescence (DF). The authors report a decrease in influence of the magnetic field on the intensity of the DF up to a change in the effect sign for anthracene with an increase in the concentration of O_2 in N,N′-dimethylformamide and no effect for pyrene and anthracene in acetonitrile. The observed changes are explained by the decrease in the quenching rate of T-states in a field with induction of 0.8 T, which contradicts the conclusions made in [5].

Frankevich and Sokolik in [7] observed the influence of magnetic field on the rate of photooxidation of crystalline tetracene. The interpretation of the mechanism was made in [8] for the anthracene-O_2 system based on the standard model of the TTA magnetic effect mechanism [1], however, the calculation took into account sharp difference between the ZFS parameters for anthracene and oxygen and the twofold degeneration of the O_2 levels in zero field due to the axial symmetry of this molecule. The theoretical dependence $\gamma(B)$ agreed well with the experimental data.

Thus, as already noted in [9], to date, somewhat contradictory experimental material has been accumulated regarding the magnetic sensitivity of the reaction T-$\Sigma_g^-(O_2)$. In [9], influence of external magnetic field on the delayed luminescence (DF and phosphorescence) of alcoholic solutions of fluorescein family dyes (fluorescein, eosin, erythrosin) with different contents of molecular oxygen was studied. In order to increase the magnetosensitive component in the total DF signal, conditions were created for effective cross annihilation of T-excitations of dyes and aromatics. The error in determining the average value of the magnetic modulation $\gamma(B) = [I_{\mathrm{DF}}(B) - I_{\mathrm{DF}}(0)]/I_{\mathrm{DF}}(0)$, where $I_{\mathrm{DF}}(B)$ and $I_{\mathrm{DF}}(0)$ — DF intensities at the signal maximum in the induction field B and zero field respectively, was 1.5−2%. A kinetic curve typical of heteroannihilation DF with pronounced maximum indicated efficient transformation of the energy of T-excitations with localization of this energy at the excited singlet level of the dye molecule. The phosphorescence signal of halofluoresceins did not change in magnetic field with induction up to 1.5 T. When molecular oxygen was introduced into the system, a sharp increase in the instantaneous intensity of DF was observed, indicating occurrence of the reaction

$$T + {}^1\Delta_g(O_2) \rightarrow S_1 + {}^3\Sigma_g^-(O_2), \qquad (2)$$

where S_1 — the first excited state of the luminophore.

The process (2) is accompanied by luminophore DF, which has the following specific features [10]. First, the glow intensity increases with an increase in the oxygen concentration in the system at a constant pump level. Second, the time dependence of intensity passes through a maximum in the microsecond range when the reactions (1) and (2) occur in oxygen-permeable systems, including solid polymer matrices. However, if these reactions occur at the phase boundary, in this time region the stage of DF signal rise is not experimentally observed [11].

It turned out that the dependences of the magnetic modulation depth of DF of eosin and erythrosin in field with induction of 1.5 T on the concentration of O_2, as well as

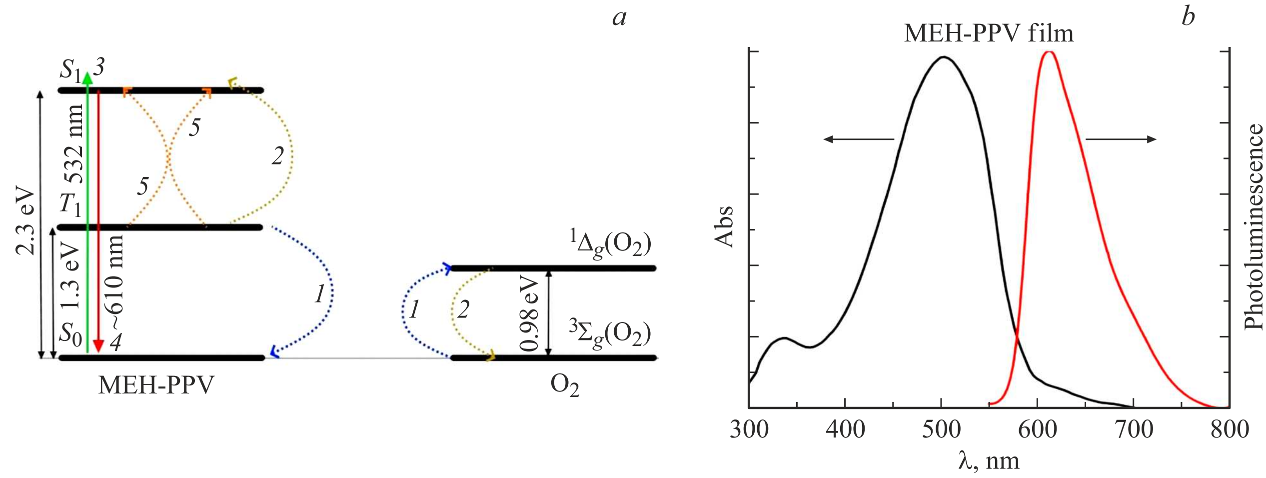

Figure 1. Diagram of the main energy states and transitions in the MEH-PPV and O_2 system responsible for magnetosensitive photoluminescence [2,13-15]. (*a*) Curve *1* — T-O_2-quenching, *2* — T-$^1\Delta_g(O_2)$—triplet exciton cross-annihilation with singlet oxygen, *3* — S_0—S_1 absorption, *4* — fluorescence, *5* — T-T-exciton annihilation. (*b*) Optical spectral properties of MEH-PPV films.

similar dependences for the fluorescein-1,2-benzanthracene and erythrosine-anthracene systems in alcoholic solutions at 293 K have a monotonically attenuating nature with an increase in the oxygen concentration in the solution. In oxygen-saturated solution (at atmospheric air pressure above its surface), the intensity of DF did not change when the magnetic field was turned on.

To explain sharp increase in instantaneous intensity of $I_{\mathrm{DF}}^{\max}$ DF of dye solutions induced by O_2 molecules, and decrease in the magnitude of the magnetic effect, the most realistic version of implementation of the non-selective in spin T-$^1\Delta_g(O_2)$-annihilation (2) was adopted. It was assumed that efficiency of T-$^1\Delta_g(O_2)$-fusion of excitations with the birth of a local S_1-state is higher than in the T-T-heteroannihilation of organic molecules. In this case T-$^1\Delta_g(O_2)$-annihilation almost completely is responsible for the DF signal of the dye, and such a process develops due to decrease in the number of acts of homo- and heterogeneous T-T-fusion.

A detailed analysis of the possible causes of the oxygen-dependent magnetic effect carried out in [9] showed that, under the conditions of the experiment, preference should be given to the reaction (2). Dominant development of T-$^1\Delta_g(O_2)$-fusion, in turn, can be due to two circumstances : deformation of electron shells in T-$^1\Delta_g(O_2)$-complex more preferable for annihilation compared to the deformation of shells in the T_{D}-T_{A}-complex, the larger value of the Franck-Condon factor for the transition of T-$^1\Delta_g(O_2) \to S_1$-$\Sigma_g^-(O_2)$. Consideration of the orbital factors for the T-$^1\Delta_g(O_2)$-fusion and TTA showed that there is the approximate equality of these quantities. Spin factor which is equal to 1 for spin-nonselective annihilation (2) and 1/9 for TTA can make a slightly larger contribution to the higher efficiency of T-$^1\Delta_g(O_2)$-fusion. As regards the difference between the Franck-Condon factors for these reactions, its presence was not established in [9].

Summarizing what has been said about the reactions T-$^1\Delta_g(O_2)$- and T-T-fusion, it should be noted that for a wide range of pairs of organic dye-aromatic hydrocarbon compounds, annihilation of O_2 singlet excitations with T-excitations of luminophores does not inferior in efficiency to the processes of direct and cross fusion of T-excitations [10–12].

The MEH-PPV molecule is characterized by the band gap $E_g \sim 2.3$ eV, and energy of triplet excitons is at the level of $T_1 \sim 1.3$ eV [16]. In solutions of toluene and benzene, polymer molecule has maximum absorption coefficient at the wavelength $\lambda_{\mathrm{exc}} = 495$ nm. The luminescence spectrum of MEH-PPV in solutions is weakly structured, and up to three peaks can usually be observed. The maximum luminescence intensity in this case falls on the wavelength $\lambda_{\mathrm{em}(0-0)} = 554$ nm — the main transition, the other two — transitions on $\lambda_{\mathrm{em}(0-1)} = 605$ nm and $\lambda_{\mathrm{em}(0-2)} = 665$ nm. The luminescence spectra of the films have an unstructured bell-like shape at room temperature and exhibit a „red shift". The (0–0) transition is strongly suppressed in this case, and the luminescence intensity maximum falls at wavelength near $\lambda_{\mathrm{em}(0-1)} \sim 615$ nm (Fig. 1, *b*) depending on the structure and presence of impurities in the material. For example, it was previously recorded that the spectra of MEH-PPV nanoparticles have not so strong „red shift" with intensity maximum at wavelength of $\lambda_{\mathrm{em}(0-1)} = 605$ nm, while for continuous films $\lambda_{\mathrm{em}(0-1)} = 614$ nm [17].

The effect of molecular oxygen on MEH-PPV is of a stepwise nature and, as a rule, begins with formation of singlet oxygen due to the quenching of triplet excitons (indicated by arrows *1* in Fig. 1, *a*).

Singlet oxygen, being a reactive form of molecular oxygen, can interact with various parts of the MEH-PPV chain. According to a number of studies, areas of the molecule with C–H bonds of the vinyl group, C=C and C–C bonds in the phenyl group, and C–O–C group are

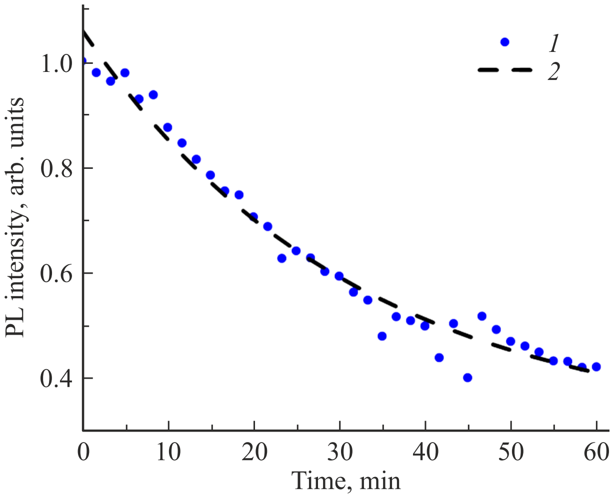

Figure 2. Decrease in the luminescence signal of MEH-PPV films due to exposure to atmospheric oxygen (*1*). The characteristic signal attenuation time according to the established monoexponential approximation (*2*) is $\tau = 31.6\,\text{min}$.

subject to photooxidation [18,19]. All of them lead to an irreversible decrease in the photoluminescence quantum yield (Fig. 2).

However, when singlet oxygen interacts with the MEH-PPV chain area in the triplet state, a cross-annihilation reaction is possible, i.e. transfer of energy from singlet oxygen to a triplet exciton, followed by transition of the exciton to the S_1-state and fluorescence without the formation of a new chemical photoproduct. This process is reflected in Fig. 1, *a* by transitions *2*. Processes of this type of generation of singlet oxygen by chromophores in solutions and in oxygen-permeable polymer films were studied earlier [9–12,20–23].

Experimental part

In this article, polymeric films of a polyphenylene vinylene derivative (MEH-PPV) with a molecular weight of $M_r \sim 150000-250000$ were used as the objects under study. Molecules of this polymer are excitonogenic and are characterized by the highest occupied molecular orbital (HOMO, $-5.3\,\text{eV}$) and the lowest vacant molecular orbital (LVMO, $-3\,\text{eV}$). To obtain films, solution of MEH-PPV polymer with a mass fraction of 0.1% in benzene was prepared. The resulting solution was deposited on glass substrates $10 \times 25\,\text{mm}$ in size. Then the samples were dried at room temperature for 2 h. Polyphenylene vinylene (MEH-PPV) was used in preparation of polymer benzene solutions in the form of powder manufactured by Sigma Aldrich. The polymer was used without purification and additional processing.

The layout of the experimental setup for observing influence of a magnetic field on the luminescence of deaerated and oxygen-saturated MEH-PPV film samples is shown in Fig. 3.

In the course of the experiment, the obtained samples of MEH-PPV films, previously placed in a quartz evacuated cell (*5*) between the EM-1 (*2*) electromagnet poles, were irradiated with ATS 53–250 (*1*) continuous laser at wavelength of 532 nm with output power of 22 mW. The luminescence signal was passed through a monochromator (*3*), which made it possible to perform spectral selection of the signal and get rid of the reflected laser radiation. Then, a signal at wavelength of 614 nm arrived at the PMT (*4*). The oscilloscope (*6*) in the recorder mode recorded the signal from PMT. A 3NVR-1D sliding vane rotary oil pump was used to deaerate the sample placed in a transparent vacuum cell. In this case, pressure in the cell was reduced to the value $\sim 0.1\,\text{kPa}$. Magnetic field induction inside the cell was measured using a DKhK-0.5A Hall sensor. Magnetic field induction varied in the range of 0–350 mT. The measurement results in the range of induction values 0–200 mT are not presented due to the significant suppression of the useful signal by noise.

Results and discussion

To observe the magnetically dependent luminescence, intensity of photoluminescence of the MEH-PPV films was modulated by the action of rectangular magnetic field pulses with a duration of 1.5–2 s. A series of such measurements was carried out at atmospheric pressure and at pressure of 0.1 kPa in an evacuated cell. The obtained modulated signals were presented as a percentage, with luminescence intensity in the absence of magnetic field taken as 100% of intensity.

Figure 4 shows oscillograms of luminescent signals from film samples of MEH-PPV polymer at atmospheric pressure and at pressure of $\sim 0.1\,\text{kPa}$ when the samples are pulsed with an external magnetic field. As can be seen in Fig. 4, *a*, MEH-PPV films at atmospheric pressure in a cell give bursts in the direction of increasing luminescence intensity due to modulation by magnetic field with amplitude of 340 mT.

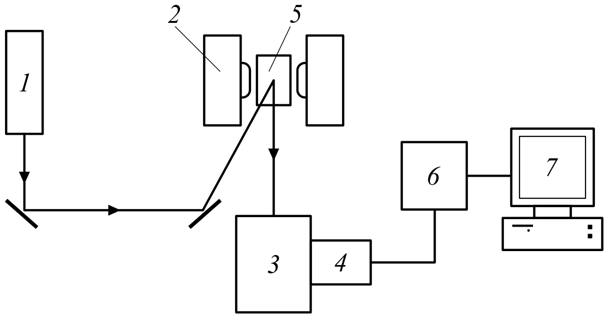

Figure 3. Layout of experimental setup. *1* — ATS 53–250 laser (radiation wavelength 532 nm; 2nd harmonic Nd^{3+}), *2* — EM-1 electromagnet, *3* — MDR-206 monochromator, *4* — PMT-84, *5* — optical evacuated sample cell, *6* — digital ACK 4106 oscilloscope, *7* — PC.

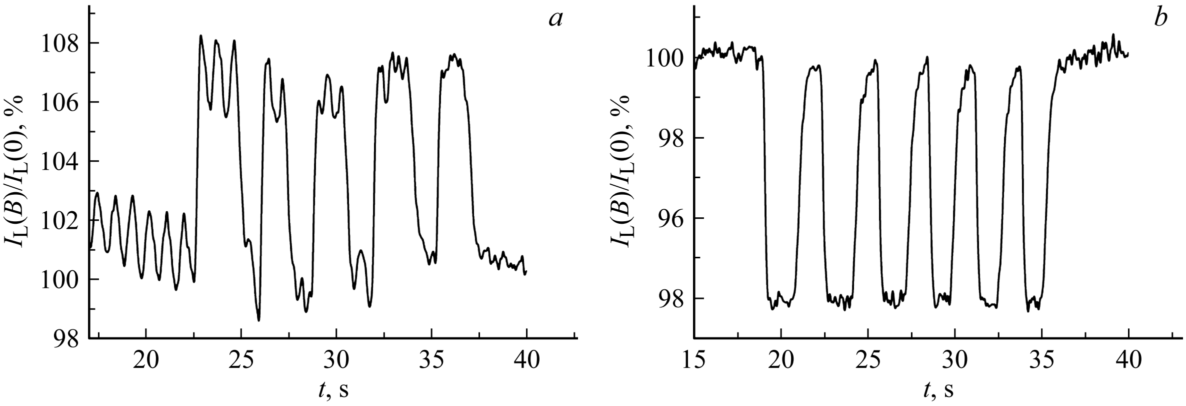

Figure 4. Oscillograms of luminescence of MEH-PPV polymer films at atmospheric pressure (*a*) and at pressure ~ 0.1 kPa (*b*), modulated by a pulsed magnetic field.

Such a phenomenon is usually called the positive effect of magnetic field influence, since an increase in the luminescence intensity occurs when an external magnetic field is applied. When the films are deaerated, effect sign reversal is observed, which manifests itself in a pulsed „subsidence" of luminescence intensity due to modulation by magnetic field with amplitude of 340 mT (Fig. 4, *b*).

Figure 5 shows plots of the luminescence modulation depth for oxygen-saturated and deoxygenated MEH-PPV films as a function of magnetic field. Experimental data of magnetic field effects (arrays of values *1* and *3*) are approximated by the curve *4* for an evacuated sample and by a plot of a quadratic function (curve *2*) for a sample at atmospheric pressure, which was the optimal approximation in this range of magnetic field induction values. These dependences allowed us to assume that the TTA process of excitons causes the negative effect (curve *4*), since under conditions of lack of oxygen, the concentration of triplet excitons increases, which, in turn, leads to an increase in the TTA probability and the often observed negative magnetic effect of the annihilation DF.

A completely different situation occurs with the positive effect of magnetic field (Fig. 5, curve *2*), i.e. effect observed in our experiment at atmospheric pressure. The very fact of the positive response of photoluminescence to the magnetic field action indicates that formation of the resulting photoresponse to the magnetic action is mainly dominated by the processes of spin-selective quenching (*1*). Note that there are no other spin-selective processes directly related to the excited singlet state of the polymer, except for the process of division of singlet excitons into two triplet excitons, which is excluded from consideration due to the lack of energy of the singlet excitation quantum, equal to 2.33 eV, while formation of two triplets during division of a singlet requires energy of about ~ 2.8 eV.

Thus, the only mediated spin-selective process remains that can cause a positive effect — this is the process of quenching (1) excitons by molecular oxygen in the ground state (T-$\Sigma_g^-(O_2)$-quenching), which results in an increase in the concentration of singlet oxygen $^1\Delta_g(O_2)$ and, consequently, the probability of nonmagnetically sensitive cross-annihilation (2) of singlet oxygen with a triplet exciton (T-$^1\Delta_g(O_2)$-annihilation, Fig. 1, *a*) and filling the singlet level S_1 of the exciton increases.

The kinetics of the population of T-excitons of luminophore in magnetic field of induction B and the concentration of singlet oxygen $n_\Delta(t)$ is determined by the equations

$$\frac{d}{dt} m_T(t) = Q_T - \frac{1}{\tau_T} n_T(t) - \big[K_\Sigma(B) n_{\text{ox}} n_T(t)$$

$$- (K_\Sigma(B) - K_\Delta) - K_\Delta) n_\Delta(t) n_T(t)\big] - K_T(B) n_T^2(t), \quad (3)$$

$$\frac{d}{dt} n_\Delta(t) = -\frac{1}{\tau_\Delta} n_\Delta(t)$$

$$- [K_\Sigma(B) + K_\Delta] n_T(t) n_\Delta(t) + K_\Sigma(B) n_{\text{ox}} n_T(t), \quad (4)$$

$$n_\Sigma(t) + n_\Delta(t) = n_{\text{ox}},$$

where $K_\Sigma(B)$ and $K_T(B)$ — magnetically dependent bimolecular constants of T-$\Sigma_g^-(O_2)$-quenching and T-T-annihilation rates; Q_T — constant density of T-states generation rate; τ_T — T-state lifetime; n_{ox} — total concentration of molecules O_2 — quenchers T-excitons in the film; τ_Δ — lifetime of excited singlet states of oxygen molecules. Note that the rate constant K_Δ does not depend on the magnetic field, because the process of T-$^1\Delta_g(O_2)$ cross-annihilation is not spin-selective, which was confirmed by direct experimental measurements in the article [9]. Under stationary conditions, i.e. at $\frac{d}{dt} n_T = \frac{d}{dt} n_\Delta = 0$, and for the inequality $K_\Sigma(B) n_{\text{ox}} n_T \gg (K_\Sigma(B) - K_\Delta) n_\Delta n_T$ (weak pumping condition, or proximity of the quenching and cross-annihilation rate constants) for the concentration of $n_T^\infty(B)$ T-molecules, from (3) we obtain

$$n_T^\infty(B) = \frac{[1+K_\Sigma(B) n_{\text{ox}} \tau_T]}{2K_T(B)\tau_T} \left[\sqrt{1+\frac{4Q_T K_T(B)\tau_T^2}{[1+K_\Sigma(B) n_{\text{ox}}\tau_T]^2}} - 1\right]. \quad (5)$$

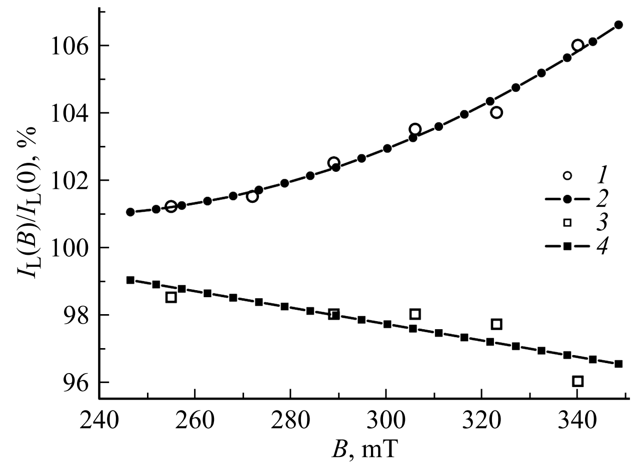

Figure 5. Relative changes in the luminescence intensity of the MEH-PPV polymer in magnetic field for oxygen-saturated (*1, 2*) and deoxygenated (*3, 4*) samples. *1* — experimental data, *2* — their approximation by a quadratic function at atmospheric pressure in a cell with a film sample, *3* — experimental data, *4* — their approximation by a linear dependence at pressure of ~ 0.1 kPa.

Substituting (5) into the stationary version of equation (4), we obtain

$$n_\Delta^\infty(B)=\frac{K_\Sigma(B)n_T^\infty(B)n_{\mathrm{ox}}\tau_\Delta}{1+(K_\Sigma(B)+K_\Delta)n_T^\infty(B)\tau_\Delta}. \tag{6}$$

For weak pump Q, it follows from (5) that

$$n_T^\infty(B)=\frac{Q_T\tau_T}{[1+K_\Sigma(B)n_{\mathrm{ox}}\tau_T]}, \tag{7}$$

and for the stationary density of singlet oxygen from (6) we obtain

$$n_\Delta^\infty(B)=\frac{Q_T\tau_T K_\Sigma(B)n_{\mathrm{ox}}\tau_\Delta}{[1+K_\Sigma(B)n_{\mathrm{ox}}\tau_T+(K_\Sigma(B)+K_\Delta)Q_T\tau_\Delta\tau_T]}. \tag{8}$$

If the magnitude of the magnetic effect is estimated based on the ratio of the intensities of $I_{\mathrm{DF}}(B)$ DF, accompanying the TTA and T-$^1\Delta_g(\mathrm{O}_2)$-cross-annihilation reactions, then for it we can write

$$\gamma_{\mathrm{DF}}(B)=\frac{I_{\mathrm{DF}}(B)}{I_{\mathrm{DF}}(0)}=$$

$$=\frac{\frac{1}{2}p_S K_T(B)[n_T^\infty(B)]^2+p_{T\Delta}n_T^\infty(B)n_\Delta^\infty(B)}{\frac{1}{2}p_S K_T(0)[n_T^\infty(0)]^2+p_{T\Delta}n_T^\infty(0)n_\Delta^\infty(0)}, \tag{9}$$

where $n_T^\infty(B)$ and $n_\Delta^\infty(B)$ are defined by expressions (5) and (6) (or (7) and (8)), and p_S and $p_{T\Delta}$ – the probabilities of local singlet excitation formation in a separate event of TTA or T-$^1\Delta_g(\mathrm{O}_2)$-cross-annihilation, respectively.

Thus, from the analysis of the obtained expressions (9) and (5), (6) we conclude that the magnetic dependence of the intensity of the annihilation DF is a complex function of the magnetic field induction B. The bimolecular rate constants $K_\Sigma(B)$ and $K_T(B)$ in the region of sufficiently large values of the field induction decrease with increasing field, the density of T-excitons in the oxygen-containing film increases, and the concentration of singlet oxygen decreases. Which of these tendencies will be decisive in the formation of the observed field dependence of the glow signal depends on the oxygen concentration in the system and pumping of Q.

Calculations of the magnetic effect taking into account the TTA and T-Δ-cross-annihilation reactions of $\gamma_{\mathrm{DF}}(B)$ based on expression (9) confirm the possibility of reversing the effect sign.

Figure 6, *a* and *b*, shows the magnetic field dependences of the intensity of delayed fluorescence with varying parameters of the mathematical model: the total concentration of molecules O_2 in the film n_{ox} and T-$^1\Delta_g(\mathrm{O}_2)$-cross-annihilation rate constant K_Δ. As can be seen in the figures, a change in the sign of the magnetic field effect can occur with a change in the value of the cross-annihilation rate constant. It can also be seen in Fig. 6, *b* that the magnetic field dependences of the DF signals are sensitive to changes in the concentration of molecules O_2.

In addition to the above results, for the purpose of a more detailed consideration, sections of the magnetic field effects were analyzed depending on the above parameters (Fig. 6, *c, d*), i.e. dependence of the maximum value of the magnetic field effect attributable to the magnetic field induction of 0.3 T on the already considered model parameters. These curves show the nature of the change in the magnetic field effects of DF of polymer samples on the total concentration n_{ox} of molecules O_2 in the film and T-$^1\Delta_g(\mathrm{O}_2)$-cross-annihilation rate constant K_Δ. As can be seen in the figures, these dependences are non-linear. With variations in the K_Δ cross-annihilation rate constant (Fig. 6, *c*), the function $\max\gamma_{\mathrm{DF}}$ is monotonically decreasing and crosses the level $\gamma_{\mathrm{DF}}=1$, and as the concentration of molecules O_2 changes (Fig. 6, *d*) — increasing with reaching the asymptote and without sign change. A value on the vertical axis equal to 1 means the absence of both positive and negative magnetic field effects. Thus, the point lying at level 1 along the vertical axis reflects the phenomenon of compensation for the decrease in triplet excitons due to TTA and their increase due to T-O_2-quenching. This phenomenon can be observed in Fig. 6, *c*.

Conclusion

Thus, as a result of the experiments performed, in the article, reversal of the effect sign of magnetic field influence on the intensity of MEH-PPV film luminescence was registered during the stage-by-stage evacuation of the cells with the samples subjected to irradiation. A theoretical model is proposed based on balance kinetic equations that take into account the formation of quasi-stationary populations of triplet excitons of the polymer and singlet oxygen during TTA exciton processes, as well as T-$^3\Sigma_g(\mathrm{O}_2)$-quenching and

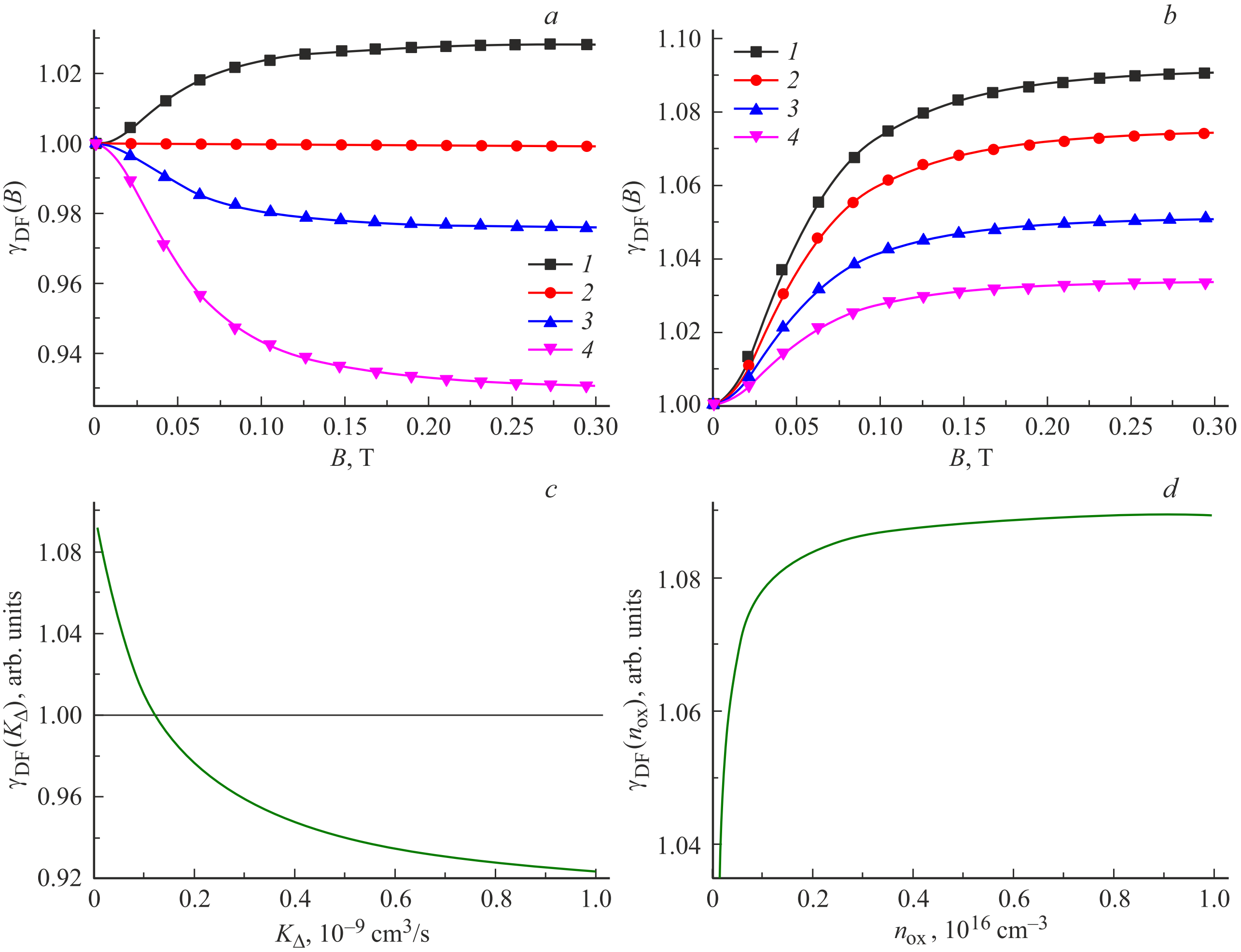

Figure 6. Magnetic field dependences of the relative intensity of DF at varying (*a*) T-$^1\Delta_g(O_2)$-cross-annihilation rate constant K_Δ (*1* — 10^{-11} cm^3/s, *2* — $7 \cdot 10^{-11}$ cm^3/s, *3* — $1.25 \cdot 10^{-10}$ cm^3 /s, *4*— $2 \cdot 10^{-10}$ cm^3/s) and (*b*) concentrations of molecules O_2 n_{ox} (*1* — $5 \cdot 10^{16}$ cm^{-3}, *2* — $7 \cdot 10^{14}$ cm^{-3}, *3* — $2 \cdot 10^{14}$ cm^{-3}, *4* — 10^{14} cm^{-3}). Dependences of the maximum value of the magnetic field effect at 0.3 T on (*c*) the T-$^1\Delta_g(O_2)$-cross-annihilation rate constant and (*d*) concentration of molecules O_2 n_{ox}.

T-$^1\Delta_g(O_2)$-cross-annihilation of electronic excitations. The model took into account that only some of the bimolecular reactions involving T-excitons were spin-selective and, for this reason, dependent on the external magnetic field. The oxygen-dependent magnetic field effects of DF of the MEH-PPV films calculated according to the theoretical model are in good agreement with the experimental results.

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