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## PECULIARITIES OF ELECTRON-EXCITATION-ENERGY TRANSFER IN CARBAZOLE-CONTAINING POLYMERS

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*Luminescence spectra of poly-N-vinylcarbazole (PVK), poly-N-epoxypropylcarbazole (PEPK), poly-N-vinyl-3-chlorocarbazole (Cl-PVK), and polystyrene (PS) films doped with bis[2-(2'-benzothienyl)-pyridinato-N,C<sup>8'</sup>](acetylacetonate) iridium [Btp<sub>2</sub>Ir(acac)] have been studied. The indicated carbazole-containing polymers are promising for the application in electroluminescence devices. The quantum yield of sensitized phosphorescence by Btp<sub>2</sub>Ir(acac) molecules in carbazole-containing polymer matrices is found to be lower than at their direct excitation in the PS matrix. The additional doping of the PVK-based composite with benzophenone, which transforms some of singlet excitons into triplet ones, diminishes the intensity of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) molecules, which testifies that the efficiency of energy transfer via singlet excitons is higher than via triplet ones. The results obtained can be explained by a competition between the process of energy transfer onto the acceptor site, on the one hand, and the processes of exciton localization at the tail energy states and the trapping of triplet excitons by the products of polymer oxidation, on the other hand. The quantum yield of sensitized phosphorescence by Btp<sub>2</sub>Ir(acac) molecules in the PVK matrix is found to be almost 1.5 times lower than in the PEPK one. A conclusion is drawn that, in the PVK matrix, the process of singlet exciton autolocalization at excimer-forming centers followed by the creation of sandwich-like excimers competes with the process of excitation energy transfer onto the acceptor.*

*Keywords:* poly-N-vinylcarbazole, poly-N-epoxypropylcarbazole, fluorescence, phosphorescence, energy transfer, singlet excitons, triplet excitons.

### 1. Introduction

The challenging character of researches dealing with the photophysical processes in luminescent photoconductive organic compounds is associated with their practical application in active layers of electroluminescent diodes and color displays [1–13]. The advantage of soluble polymers in comparison with the application of low-molecular compounds consists in a possibility of the layer deposition immediately from solutions, e.g., by making use of high-technology methods of jet and screen printing [7–10], which not only significantly reduces the cost price of products, but

also allows panels with a large area, including flexible substrates, to be manufactured. For the deposition of several functional layers, a method was developed for the preparation of aqueous suspensions of photoconductive polymers [14]. This method makes it possible to prevent the damage of already formed layers by the solvent, when a new layer is deposited.

For practical applications, polymer white-light-emitting diodes are of particular interest. Here, white light is prepared by the mixing of three basic colors – red, green, and blue – in a certain proportion. For this purpose, devices with two or three active layers deposited onto different substrates and emitting light with different colors, as well as structures with

rows of pixels arranged on a common substrate, have been developed [6]. However, such devices are rather complicated and expensive. For a device to possess only one active radiation layer, fluorescent or phosphorescent doping impurities were proposed to be introduced into a conducting polymer that emits blue or shorter-wave light [1, 4, 9–11, 15].

According to spin statistics data [2, 10, 16], three times as many triplet excitons as singlet ones are formed at the recombination of charge carriers injected from electrodes. In order to transform these triplet excitons into light quanta, organic complexes of heavy metals were proposed to be applied as doping impurities. Owing to the strong spin-orbit interaction induced by the metal atom—this interaction mixes the singlet and triplet states—the quantum yield of phosphorescence  $\Phi_{Ph}$  increases significantly in those molecules, which are called triplet (phosphorescent) emitters [2, 10]. For instance, for the solid solution of  $Btp_2Ir(acac)$  in 4,4'-bis(N-carbazolyl)-diphenyl at room temperature,  $\Phi_{Ph} = 0.51$  [17]. The external electroluminescence quantum yield of a diode with an active PVK layer equals only 0.005% [3]. But, after the  $Btp_2Ir(acac)$  doping impurity has been introduced into the layer at the concentration  $C = 5$  wt%, the quantum yield increases to 2.1% [4].

The PVK and PEPK polymers belong to photoconductive polymers that are the most studied and widely used in practice. They combine such technologically important properties as the good solubility in organic solvents, the ability of film formation, and the optical transparency. Carbazole groups play the role of chromophores in both polymers, but the structures of their main chains are different. In the PVK macromolecule, the lateral carbazole groups are attached to every second carbon atom in the main chain, which favors the formation of intramolecular and intermolecular sandwich-excimer. The formation of such excimers is preceded by the migration of singlet excitons both along the chain and from one chain to another, with a subsequent localization at the excimer-forming sites [16, 18–20]. Unlike PVK, monomeric links in PEPK are interconnected in different ways, the carbazole groups are arranged chaotically, and the average distance between them is larger. As a result, the excimer fluorescence for PEPK is absent [21]. Furthermore, the PEPK molecule consists of only four to five monomer links, so that the

migration of excitons over long distances is provided by their transfer between chains.

In our previous papers [22, 23], we showed that, in the PEPK matrix, the energy transfer by singlet excitons onto the triplet emitter occurs more effectively than by triplet ones. Since PVK is widely used as a basis for polymer organic light emitting diodes [1–4, 6–11], it is reasonable to analyze the relationship between the structures of the PVK and PEPK macromolecules, on the one hand, and the intensity of the sensitized phosphorescence of the triplet emitter. For this purpose, we measured the luminescence spectra of pure PVK, Cl-PVK, and PEPK films, as well as the spectra of PVK, Cl-PVK, and PEPK films with the  $Btp_2Ir(acac)$  doping admixture, and studied the spectra of PVK films with two admixtures,  $Btp_2Ir(acac)$  and benzophenone. In addition, we measured the quantum yield of phosphorescence  $\Phi_{Ph}$  for  $Btp_2Ir(acac)$  molecules in the PS and carbazol-containing polymer films.

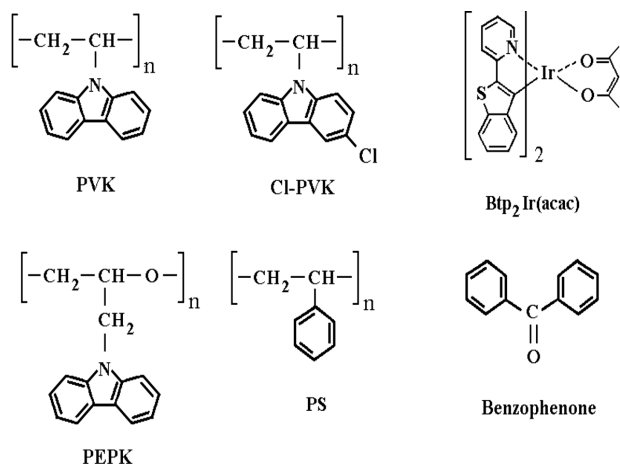
## 2. Experimental Technique

The PS (BASF), PVK (Sigma-Aldrich), PEPK, and Cl-PVK (Research Institute for Electrophotography, Vilnius) polymers, as well as the  $Btp_2Ir(acac)$  (American Dye Source Inc., USA) and benzophenone (Sigma-Aldrich) preparations, were dissolved separately in tetrahydrofuran to the polymer concentrations  $C = 5 \div 10$  wt%. Then they were mixed and kept at room temperature for several hours. The chemical formulas of polymers and impurities are shown in Fig. 1.

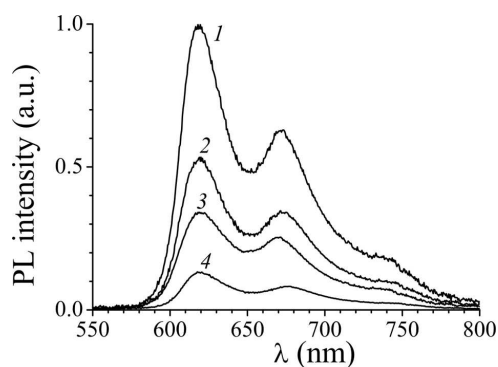
Films 20–30  $\mu m$  in thickness were deposited by pouring out the solutions onto fused quartz substrates. Then the films were dried at room temperature.

The luminescence spectra were excited with the help of radiation emitted by a high-pressure mercury lamp DRSh-250-3 and passed through glass absorption filters for the line group  $\lambda_{exc} = 313$  nm or  $\lambda_{exc} = 436$  nm. The spectra were measured on a spectrometer SDL-1.

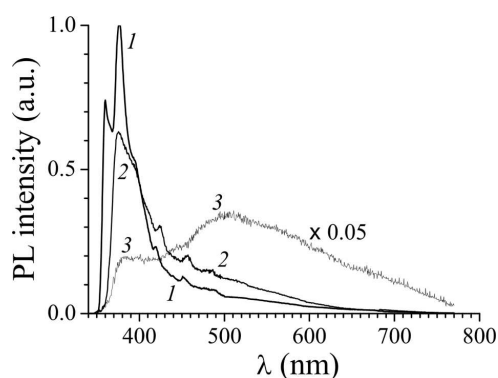
All measurements were performed at temperatures  $T = 5 \div 295$  K in an optical helium cryostat with a system of automatic temperature regulation and stabilization, which was developed and manufactured at the Institute of Physics of the National Academy of Sciences of Ukraine (Kyiv). The absolute magnitude



**Fig. 1.** Chemical formulas of the examined polymers and impurities



**Fig. 2.** Phosphorescence spectra of the PS (curve 1), PEPK (curve 2), PVK (curve 3), and Cl-PVK (curve 4) films with the Btp<sub>2</sub>Ir(acac) doping admixture (to the concentration  $C = 3$  wt%). The spectra were measured under identical excitation and registration conditions:  $\lambda_{\text{exc}} = 313$  nm,  $T = 295$  K



**Fig. 3.** Luminescence spectra of the PEPK (curve 1), PVK (curve 2), and Cl-PVK (curve 3) films. The spectra were measured under identical excitation and registration conditions:  $\lambda_{\text{exc}} = 313$  nm,  $T = 5$  K

of the fluorescence quantum yield  $\Phi_{\text{F1}}$  at the temperature  $T = 295$  K was determined by comparing the integral fluorescence intensities of the specimen and the reference solution of tri-*p*-tolylamine in toluene ( $C = 10^{-4}$  M), for which  $\Phi_{\text{F1}} \approx 0.045$  [24]. The measurement accuracy was  $\pm 10\%$ .

### 3. Experimental Results

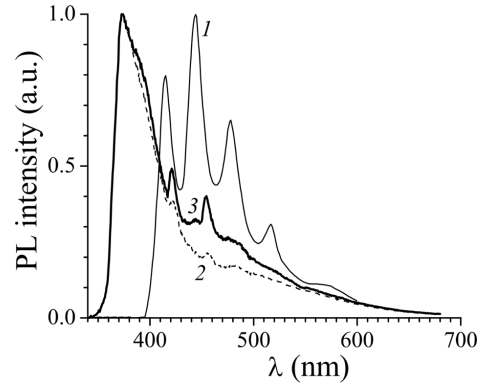
Owing to the strong spin-orbit interaction induced by the iridium atom, after the Btp<sub>2</sub>Ir(acac) molecule has absorbed excitation light, the probability of intercombination conversion  $S_1 \rightarrow T_1$  (from the first excited singlet state  $S_1$  into the triplet one  $T_1$ ) equals 100%, and the molecule itself only phosphoresces [25,26]. At room temperature, the phosphorescence spectrum of the Btp<sub>2</sub>Ir(acac) solution in PS ( $C = 3$  wt%) consists of three bands with maxima at  $\lambda_{\text{max}} \approx 620$ , 670, and 740 nm (Fig. 2, curve 1). After replacing the PS matrix by the PEPK, PVK, or Cl-PVK one, the positions of the maxima of phosphorescence bands do not change, but their intensity significantly decreases (curves 2–4), and the quantum yields equal  $\Phi_{\text{Ph}} \approx 0.50$ , 0.27, 0.20, or 0.07 in the case of PS, PEPK, PVK, or Cl-PVK matrix, respectively.

The luminescence spectra of pure PEPK, PVK, and Cl-PVK films registered at the temperature  $T = 5$  K are shown in Fig. 3. In the PEPK spectrum, three broad fluorescence bands at  $\lambda_{\text{max}} \approx 360$ , 375, and 390 nm, as well as a structural phosphorescence band starting from  $\lambda_{\text{max}} \approx 419$  nm (curve 1), can be distinguished. They are associated with the radiative transitions  $S_1 \rightarrow S_0$  and  $T_1 \rightarrow S_0$  in the lateral carbazole groups [21]. At the same time, the fluorescence spectrum of the PVK film consists of only one wide band with  $\lambda_{\text{max}} \approx 375$  nm, whereas the structural phosphorescence spectrum begins at  $\lambda_{\text{max}} \approx 424$  nm (curve 2). The indicated fluorescence bands are connected with the emission from traps of the structural origin, which are formed by two parallel carbazole groups that overlap each other only partially. This is the so-called second excimer [18–20]. In addition, the spectra of the examined PEPK and PVK films demonstrate a broad structureless phosphorescence band in the green spectral interval. This band is associated with oxidation products that are always present in carbazol-containing polymers [27]. The spectrum of the Cl-PVK film consists of a broad structureless fluorescence band with

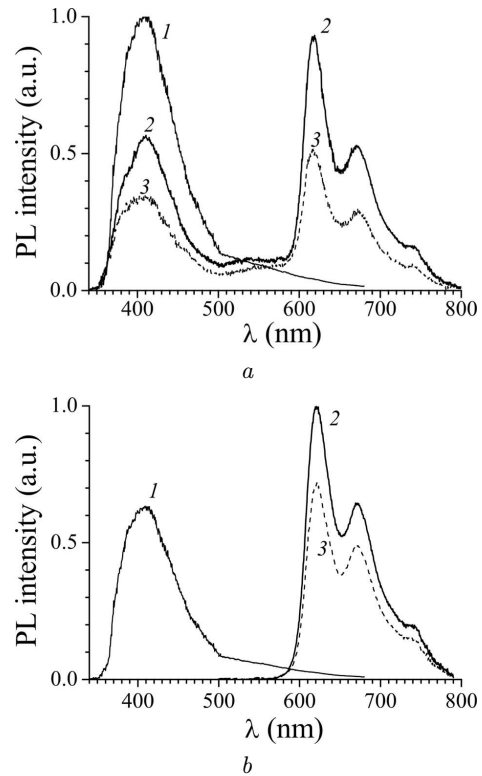
$\lambda_{\max} \approx 380$  nm and a phosphorescence band with  $\lambda_{\max} \approx 500$  nm (curve 3). Unlike the PEPK and PVK films, for which  $\Phi_{\text{Ph}}/\Phi_{\text{F1}} \approx 0.03$ , this ratio for the Cl-PVK film equals  $\Phi_{\text{Ph}}/\Phi_{\text{F1}} \approx 1.4$ . Such an increase of the ratio  $\Phi_{\text{Ph}}/\Phi_{\text{F1}}$  results from the growth of the probability of intercombination transitions  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  under the influence of the internal heavy chlorine atom [28]. At room temperature, the fluorescence quantum yield  $\Phi_{\text{F1}} \approx 0.10$ , 0.11, and 0.01 for the PVK, PEPK, and Cl-PVK films, respectively.

The PS polymer does not absorb light with  $\lambda_{\text{exc}} = 313$  nm. Therefore, the state  $T_1$  of the Btp<sub>2</sub>Ir(acac) molecule becomes populated only as a result of direct photoexcitation followed by the intercombination conversion  $S_1 \rightarrow T_1$ . Unlike the case of PS matrix, the impurities in the PEPK, PVK, and Cl-PVK matrices are mainly excited owing to the energy transfer from the matrix. The indicated polymer matrices both fluoresced and phosphorylated, so that the excitation energy was transferred by both singlet and triplet excitons. But, in the case of Cl-PVK matrix, the magnitude of  $\Phi_{\text{Ph}}$  was almost 1.5 times higher than that of  $\Phi_{\text{F1}}$ . At the same time, the quantum yield  $\Phi_{\text{Ph}}$  of sensitized phosphorescence of the Btp<sub>2</sub>Ir(acac) molecule was three times as lower as that in the PVK matrix. Therefore, we may assume that the energy transfer by singlet excitons in the PVK and Cl-PVK matrices is higher than the energy transfer by triplet ones. This assumption was made in our previous work [23] for the matrices of PEPK and its dihalogen-substituted analogs.

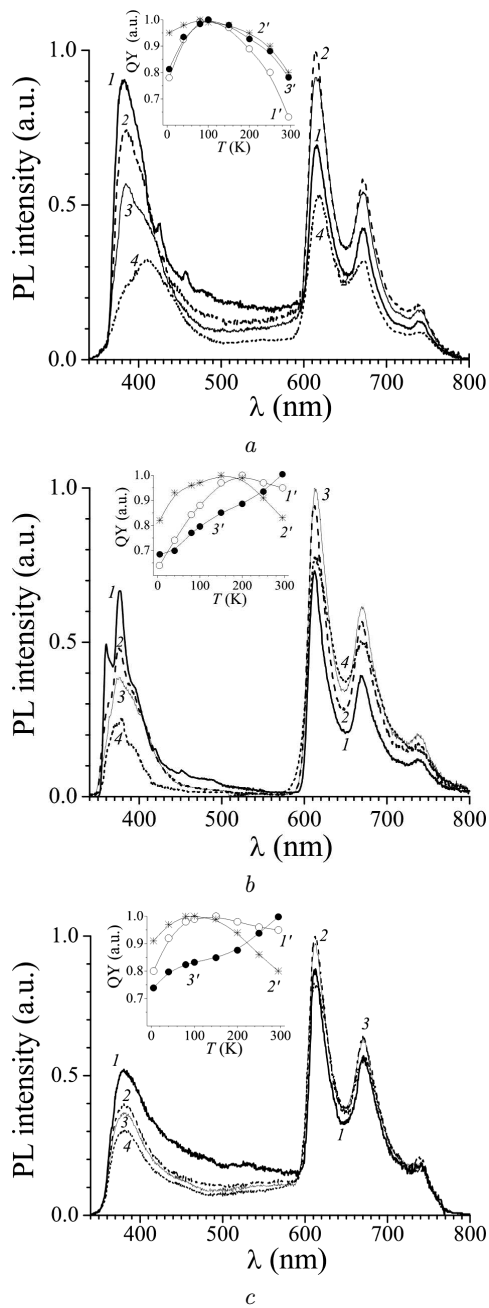
In order to prove this assumption, we compared the intensity of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) molecules in two matrices: pure PVK and PVK with an admixture of benzophenone. Figure 4 demonstrates the luminescence spectra registered at the temperature  $T = 5$  K for benzophenone in PS, for films of pure PVK, and for PVK films with an admixture of benzophenone. After the photoexcitation of a benzophenone molecule, the intercombination conversion  $S_1 \rightarrow T_1$  takes place with a probability of about 100% [28], and the molecule only phosphoresces. The spectrum of this phosphorescence in the PS matrix begins from a band with  $\lambda_{\max} \approx 415$  nm (curve 1), and the energy of the benzophenone level  $T_1$  is equal to  $E_T \approx 24100$  cm<sup>-1</sup>. Since the distance between the  $S_1$  and  $T_1$  levels in benzophenone is  $E_{ST} \approx 1600$  cm<sup>-1</sup> [28], the level  $S_1$  in benzophe-



**Fig. 4.** Normalized luminescence spectra of the benzophenone solution in PS (the concentration  $C = 5$  wt%, curve 1), the pure PVK film (curve 2), and the PVK film with the benzophenone admixture (the concentration  $C = 5$  wt%, curve 3). The spectra were measured under identical excitation and registration conditions:  $\lambda_{\text{exc}} = 313$  nm,  $T = 5$  K



**Fig. 5.** Luminescence spectra of the pure PVK film (curve 1), the PVK film with the Btp<sub>2</sub>Ir(acac) admixture (curve 2), and the PVK film with the Btp<sub>2</sub>Ir(acac) and benzophenone admixtures (curve 3). The benzophenone concentration  $C = 5$  wt%; the Btp<sub>2</sub>Ir(acac) concentration  $C = 0.1$  wt% (a) and 3 wt% (b). The spectra were measured under identical excitation and registration conditions:  $\lambda_{\text{exc}} = 313$  nm,  $T = 295$  K



**Fig. 6.** Luminescence spectra (the excitation wavelength  $\lambda_{\text{exc}} = 313$  nm) of the PVK (a), PEPK (b), and Cl-PVK (c) films with the Btp<sub>2</sub>Ir(acac) admixture (to the concentration  $C = 0.1$  wt%) at various temperatures  $T = 5$  (1), 100 (2), 150 (3), and 295 K (4). The temperature dependences of the relative quantum yield of the Btp<sub>2</sub>Ir(acac) sensitized phosphorescence (curve 1'), the relative molecular quantum yield of the Btp<sub>2</sub>Ir(acac) phosphorescence (curve 2'), and the energy transfer efficiency (curve 3') are shown in the insets

none is located by about  $1000 \text{ cm}^{-1}$  lower than the level  $S_1$  in PVK ( $E_S \approx 25700$  and  $26700 \text{ cm}^{-1}$ , respectively). Hence, if the PVK film with an admixture of benzophenone is excited, the energy of a singlet exciton can be transferred to the benzophenone molecule with the subsequent intercombination conversion  $S_1 \rightarrow T_1$  in the molecule. The energy of the level  $T_1$  of benzophenone in the PVK matrix is about  $500 \text{ cm}^{-1}$  higher than the energy of the level  $T_1$  of PVK ( $E_T \approx 23600 \text{ cm}^{-1}$ ). Therefore, the transfer of the triplet excitation energy from benzophenone to the PVK carbazole group is performed. As a result, some of singlet excitons are transformed into triplet ones, which is testified by the growth of the relative intensity of the PVK phosphorescence spectrum after the introduction of the benzophenone impurity (curves 2 and 3).

When introducing the Btp<sub>2</sub>Ir(acac) impurity into the PVK film to the concentration  $C = 0.1$  wt%, the matrix fluorescence intensity undergoes a twofold reduction, and there appears the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) (Fig. 5, a; curves 1 and 2). In the case where two additives are added to PVK–Btp<sub>2</sub>Ir(acac) at the concentration  $C = 0.1$  wt% and benzophenone at  $C = 5$  wt%—not only the matrix fluorescence intensity decreases by 1.5 times, but also the sensitized phosphorescence intensity of Btp<sub>2</sub>Ir(acac) diminishes by almost a factor of two (Fig. 5, a; curve 3). When the concentration of Btp<sub>2</sub>Ir(acac) increases to  $C = 3$  wt%, the matrix fluorescence is completely quenched, and only the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) is observed (Fig. 5, b; curves 1 and 2). An additional introduction of benzophenone to the concentration  $C = 5$  wt% stimulates an intensity reduction of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) by almost 1.5 times (Fig. 5, b; curve 3). Thus, after some of the singlet excitons in PVK have been transformed into triplet ones by the benzophenone impurity molecules, the intensity of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) decreases appreciably.

The luminescence spectra ( $\lambda_{\text{exc}} = 313$  nm) of the PVK, PEPK, and Cl-PVK films doped with the Btp<sub>2</sub>Ir(acac) admixture to the concentration  $C = 0.1$  wt%, which were registered in the temperature interval  $T = 5 \div 295$  K, are shown in Fig. 6. One can see that, with the temperature growth, the intensity of the matrix radiation emission monotonically decreases. At the same time, together with a decrease

of the intensity of the band at  $\lambda_{\max} \approx 375$  nm in the fluorescence spectrum of the PVK matrix, the band of sandwich-exciters at  $\lambda_{\max} \approx 405$  nm becomes more intense (Fig. 6, *a*; curves 1 to 4).

We have revealed that, unlike the fluorescence bands of the matrix, the band intensities of sensitized phosphorescence of the impurity vary in a complicated manner, when heating in the temperature interval  $T = 5 \div 295$  K. The temperature dependences of the quantum yield of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac),  $\Phi_{\text{Ph}}^{\text{sens}}$ , the molecular quantum yield of this admixture at a direct excitation with light with  $\lambda_{\text{exc}} = 436$  nm,  $\Phi_{\text{Ph}}^{\text{mol}}$ , and their ratio  $\Phi_{\text{Ph}}^{\text{sens}}/\Phi_{\text{Ph}}^{\text{mol}}$  in the PVK, PEPK, and Cl-PVK matrices are depicted in Fig. 6 (panels *a* to *c*, insets, curves 1' to 3'). It is evident that, when heating above 5 K, the values of  $\Phi_{\text{Ph}}^{\text{sens}}$  firstly increase by 20–35% for all polymer matrices. If the temperature grows further to 295 K, the indicated values decrease by almost 40% for the PVK matrix, and only by 10% for the PEPK and Cl-PVK ones. In so doing, the values of  $\Phi_{\text{Ph}}^{\text{mol}}$  firstly grow by 5–20% and then fall by 20%. As a result, in the case of PVK matrix, the ratio  $\Phi_{\text{Ph}}^{\text{sens}}(T)/\Phi_{\text{Ph}}^{\text{mol}}(T)$ , which describes the temperature dependence of the energy transfer efficiency, firstly – when heating to about 100 K – increases by about 10% and then – as the temperature grows further to room one – decreases by about 20%. At the same time, for the PEPK and Cl-PVK matrices, the indicated ratio monotonically increases by about 30%, when heating in the interval  $T = 5 \div 295$  K.

#### 4. Discussion of Experimental Results

From the results obtained, it follows that the impurity molecules Btp<sub>2</sub>Ir(acac) play the role of acceptors of singlet and triplet excitons in the PVK, PEPK, and Cl-PVK matrices. If the distance between donor's chromophore groups and the acceptor molecules is several times larger than the sum of their van der Waals radii, then the radiationless energy transfer for dipole-allowed transitions takes place owing to the resonance dipole-dipole interaction, i.e. following the Förster mechanism [16]. In this case, the spin state of the molecules is preserved, and only the singlet-singlet transfer is allowed. If the donor and acceptor molecules approach one another so that their molecular orbitals become partially overlapped, then the exchange electron interaction dominates, and the en-

ergy transfer is described in the framework of the Dexter theory [16]. In this case, the total spin of the system is preserved, and both the singlet-singlet and triplet-triplet energy transfers are allowed.

The rate constant of energy transfer following the Förster mechanism is directly proportional to  $(R_0/R_{\text{DA}})^6$ , where  $R_0$  is the critical transfer radius, and  $R_{\text{DA}}$  the distance between the donor and the acceptor. The value of  $R_0$  is given by the expression [16, 26]

$$R_0^6 = \frac{9000 \chi^2 \ln 10}{128 \pi^5 N_0 n^4} \Phi_{\text{D}} \int F_{\text{D}}(\nu) \varepsilon_{\text{A}}(\nu) \frac{d\nu}{\nu^4}. \quad (1)$$

Here,  $\chi^2$  is the orientational factor ( $\chi^2 = 2/3$  for the randomly oriented donor and acceptor),  $N_0$  the Avogadro constant,  $\Phi_{\text{D}}$  the fluorescence quantum yield of the donor,  $n \approx 1.62$  [29] is the refractive index of the basis,  $F_{\text{D}}(\nu)$  the normalized fluorescence spectrum of the donor (i.e.  $\int F_{\text{D}}(\nu) d\nu = 1$ ),  $\varepsilon_{\text{A}}(\nu)$  the molar extinction coefficient of the acceptor, and  $\nu$  the wave number. On the basis of the data for the absorption by Btp<sub>2</sub>Ir(acac) [18] and the polymer fluorescence, we calculated that, at room temperature,  $R_0 \approx 2.2$  and 2.3 nm for the PVK and PEPK matrices, respectively. It is worth noting that the value of  $R_0$  obtained by us for the Btp<sub>2</sub>Ir(acac) molecules in the PVK matrix was confirmed in work [30].

The Förster mechanism is efficient provided that  $R_{\text{DA}} \leq R_0$ . If the acceptor molecules are arranged uniformly (as was found for Btp<sub>2</sub>Ir(acac) [26]), each of them is surrounded by a sphere, and the concentration is measured in mole units, then the radius of this sphere (in nanometers) equals [15, 22, 23]

$$R_{\text{DA}} = 10^7 \left( \frac{3}{4\pi N_0 C} \right)^{1/3} = \frac{0.735}{\sqrt[3]{C}}. \quad (2)$$

At the concentrations  $C = 0.1 \div 3$  wt%, i.e. at  $C = (0.14 \div 4.23) \times 10^{-2}$  M, we have  $R_{\text{DA}} = 2.1 \div 6.6$  nm, so that the distance between the donor and the acceptor can exceed  $R_0$ . Therefore, the energy transfer of a singlet exciton takes place in two stages: at first, the exciton migrates; and when the distance to the acceptor diminishes to  $R_0$ , the energy is transferred to the acceptor with a probability of 50%.

Since the polymers that are analyzed in this work belong to disordered systems, the energy states of excitons in them are characterized by a certain energy distribution. The motion of excitons has a hopping

character and is accompanied by the relaxation to low-energy states [31]. As was established in our previous work dealing with the matrices of PEPK and its dihalogen-substituted analogs [22], some of singlet and triplet excitons in the course of migration become localized at the tail energy states, which are the lowest by energy. Therefore, if the PS matrix is substituted by a carbazol-containing polymer, the value of  $\Phi_{\text{Ph}}$  for the Btp<sub>2</sub>Ir(acac) molecule diminishes.

When transferring the energy to the Btp<sub>2</sub>Ir(acac) molecule in the PVK, PEPK, and Cl-PVK matrices by a singlet exciton and provided that  $R_{\text{DA}} > R_0$ , the exciton overcomes only some part of its path by the migration mechanism. When the value of  $R_{\text{DA}}$  decreases to  $R_0$ , the energy is transferred to the acceptor with a probability of 50%. In turn, when the energy is transferred via a short-acting exchange electron interaction, the triplet exciton overcomes all its path to the acceptor as a result of the migration. It is known that carbazole-containing polymers always contain oxidation products, which form deep traps for triplet excitons [27]. The probability of the localization of excitons in tail states, as well as their capture by deep traps, increases with the migration path. As a result, the efficiency of the energy transfer by singlet excitons in PVK, as well as in PEPK [23], is higher than by triplet ones. For the Btp<sub>2</sub>Ir(acac) molecules in the Cl-PVK matrix, the value of  $R_0$  is more than twice lower than that in the PVK matrix, and, when transferring the energy, the singlet excitons migrate over a longer distance than in PVK. Therefore, the value of  $\Phi_{\text{Ph}}$  for the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) molecules in the Cl-PVK matrix is smaller than the corresponding value in the case of PVK matrix.

In order to elucidate why the value of  $\Phi_{\text{Ph}}^{\text{sens}}$  for the Btp<sub>2</sub>Ir(acac) molecule in the PVK matrix at room temperature is lower than its counterpart in the case of PERK matrix (Fig. 2; curves 2 and 3), let us consider the results of researches concerning the temperature dependence of the energy transfer efficiency in the PVK, PEPK, and Cl-PVK matrices. Since the motion of excitons in disordered systems has a jump-like character – note that, for a jump into a state with a higher energy than the initial one, some activation energy is required [31] – then the path length of singlet and triplet excitons should increase with the temperature. Accordingly, the probability for excitons to come closer to the acceptor, as well as the efficiency of the energy transfer by singlet and triplet

excitons to the acceptor, has to increase, which is observed in the spectra of sensitized phosphorescence of the Btp<sub>2</sub>Ir(acac) molecule in the RERK and Cl-PVK matrices (Fig. 6; panels *b* and *c*, insets, curves 3')

In contrast to the PEPK and Cl-PVK matrices, the efficiency of the energy transfer to a Btp<sub>2</sub>Ir(acac) molecule in the PVK matrix decreases with the temperature growth in the interval  $T = 100 \div 295$  K (Fig. 6; panel *a*, inset, curve 3'). A similar temperature dependence of the energy transfer efficiency was observed earlier [32] for the sensitized fluorescence of rubrene in the PVK matrix. The obtained data testify that, in the course of migration process, singlet excitons are captured by deep traps, and their path length decreases. Moreover, the number of trapped excitons increases with the temperature. The role of such traps is most likely played by excimer-forming centers, the concentration of which amounts about  $10^{-3}$  centers per monomeric link [16, 20]. When a singlet exciton is captured by such a center, it undergoes the autolocalization, so that a sandwich-like excimer is formed, which can exist only in the excited state. After the exciton has been autolocalized, the energy transfer to the acceptor is possible only following the Förster mechanism. The proposed interpretation is favored by the fact that the intensification of the fluorescence band of a sandwich-excimer and a reduction of the ratio  $\Phi_{\text{Ph}}^{\text{sens}}(T)/\Phi_{\text{Ph}}^{\text{mol}}(T)$  take place in the same temperature interval. Thus, when heating in the interval  $T = 100 \div 295$  K, the quantum yield of the sensitized phosphorescence of the Btp<sub>2</sub>Ir(acac) acceptor in the PVK matrix decreases not only due to the drop of the  $\Phi_{\text{Ph}}^{\text{mol}}$  value, but also because the efficiency of the singlet-exciton energy transfer to the acceptor decreases.

## 5. Conclusions

In this work, it is found that the phosphorescence quantum yield of the Btp<sub>2</sub>Ir(acac) acceptor molecules in the PEPK, PVK, and Cl-PVK matrices, when they are excited by the energy transfer with the help of singlet and triplet excitons, is lower than if they are directly excited in the PS matrix. Furthermore, if PVK, which has been previously doped with Btp<sub>2</sub>Ir(acac) molecules, is additionally doped with benzophenone molecules, which transform some of singlet excitons into triplet ones, the intensity of the sensitized phosphorescence of Btp<sub>2</sub>Ir(acac) also decreases. This means that the efficiency of the exci-

tation energy transfer by singlet excitons in PVK is higher than by triplet excitons. We explain these results by supposing that, in the course of migration process, some of excitons become localized at the tail energy states, whereas triplet excitons are also captured by deep traps that are formed by products of the carbazole group oxidation.

From the analysis of the temperature dependences of the relative phosphorescence quantum yield of Btp<sub>2</sub>Ir(acac) molecules at their direct excitation and their sensitized phosphorescence in the matrices of carbazole-containing polymers, it follows that the path lengths of singlet and triplet excitons in the PEPK and Cl-PVK matrices increase with the temperature, and, accordingly, the energy transfer efficiency increases as well. At the same time, the path length of singlet excitons in the PVK matrix decreases at higher temperatures as a result of the exciton autolocalization at excimer-forming centers. Therefore, at room temperature, the quantum yield of the sensitized phosphorescence of a Btp<sub>2</sub>Ir(acac) molecule in the PVK matrix is almost 1.5 times lower than that in the PEPK matrix. In other words, PEPK is more suitable to serve as the basis of polymer electroluminescent devices.

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ОСОБЛИВОСТІ ПЕРЕНОСУ  
ЕНЕРГІЇ ЕЛЕКТРОННОГО ЗБУДЖЕННЯ  
В КАРБАЗОЛВМІСНИХ ПОЛІМЕРАХ

Резюме

Досліджено спектри люмінесценції плівок полі-N-вініл-карбазолу (PVK), полі-N-епоксипропілкарбазолу (PEPK), полі-N-вініл-3-хлоркарбазолу (Cl-PVK) і полістиролу (PS) з домішкою біс[2-(2'-бензотієні)-піридинато-N,C<sup>3'</sup>](ацетилацетонату) ірідію (Vtr<sub>2</sub>Ir(acac)). Зазначені карбазолвмісні полімери перспективні для практичного використання в електролюмінесцентних пристроях. Встановлено, що квантовий вихід сенсibilізованої фосфоресценції молекул Vtr<sub>2</sub>Ir(acac) в матриці карбазолвмісного полімеру нижчий, ніж при їх прямому збудженні в PS. Показано, що після введення в PVK з домішкою Vtr<sub>2</sub>Ir(acac) молекул бензофенону, який трансформує частину синглетних екситонів у триплетні, інтенсивність сенсibilізованої фосфоресценції Vtr<sub>2</sub>Ir(acac) зменшується, тобто ефективність переносу енергії синглетними екситонами вище, ніж триплетними. Ці результати ми пояснюємо тим, що з переносом енергії на акцептор конкурують процеси локалізації екситонів у хвостових енергетичних станах та захоплення триплетних екситонів продуктами окислення полімерів. Виявлено, що квантовий вихід сенсibilізованої фосфоресценції Vtr<sub>2</sub>Ir(acac) в матриці PVK майже у півтора раза нижчий, ніж у PEPK. Зроблено висновок про те, що у матриці PVK процес автолокалізації синглетних екситонів в ексимероутворюючих центрах та утворення сандвіч-подібних ексимерів конкурує з переносом енергії збудження на акцептор.