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COMPARISONS OF THE EFFICIENCY OF EXCITATION ENERGY TRANSFER BY SINGLET AND TRIPLET EXCITONS IN CARBAZOLYL-CONTAINING POLYMERS

Luminescence spectra of poly-N-epoxypropylcarbazole (PEPC), poly-N-epoxypropyl-3,6-dichlorocarbazole (DCIPEPC), and poly-N-epoxypropyl-3,6-dibromocarbazole (DBrPEPC) films, both pure and with the bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}](acetylacetonate) iridium (Btp₂Ir(acac)) admixture, polystyrene (PS) films with the Btp₂Ir(acac) admixture, and composite films of PEPC with the benzophenone and Btp₂Ir(acac) admixtures have been studied. Those polymers are promising for their application in optoelectronic devices. It is found that, in the case of PEPC matrix, the excitation energy is transferred both via singlet excitons (through migration and long-range dipole-dipole interaction) and triplet ones (due to the migration and short-range electron exchange interaction). At the same time, in the films based on phosphorescent DBrPEPC, the energy transfer is only provided by triplet excitons. It is found that the quantum yield of the sensitized phosphorescence for Btp₂Ir(acac) molecules in the carbazolyl-containing polymer matrix is lower than that under their direct excitation in the PS matrix. For the PEPC-based composite, this parameter is found to be three and five times higher than that for the DCIPEPC and DBrPEPC matrices, respectively. The additional doping of the PEPC-based composite with benzophenone gave rise to the transformation of some singlet excitons into triplet ones and, as a result, to a reduction of the sensitized Btp₂Ir(acac) phosphorescence intensity. A conclusion is drawn that, during the migration, some of both singlet and triplet excitons became localized in the tail energy states, and a certain fraction of triplet excitons is trapped by polymer oxidation products.

Keywords: carbazolyl-containing polymers, sensitized phosphorescence, energy transfer, singlet and triplet excitons.

1. Introduction

Photoconducting soluble polymers are extremely promising for their practical application as a basis of light-emitting diodes [1–7] and color displays [8, 9]. This fact is associated with a possibility to deposit layers directly from solutions by watering, as well as using hi-tech methods of ink-jet [7] and screen

[5, 8] printing, which considerably reduces the cost of products in comparison with the case where organic compounds with a low molecular weight are deposited in vacuum [10].

The development of polymer light-emitting diodes for “white” light – for example, for the illumination in liquid-crystal displays or as light sources – is challenging. To obtain “white” light, three (red, green, and blue) or two (yellow and red) colors have to be

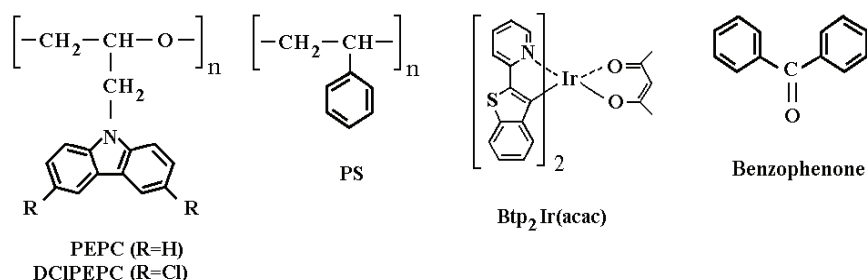


Fig. 1. Chemical formulas of researched polymers and admixtures

mixed. For this purpose, a conducting polymer, which emits blue or more short-wave light, is doped with fluorescent or phosphorescent admixtures [1, 2, 5].

From a statistical analysis [11], it follows that 3/4 of excitons that are created at the recombination of injected charge carriers are triplet ones. Without special means, they disappear nonradiatively at room temperature. Therefore, in order to enhance the quantum efficiency of light-emitting diodes, phosphorescent admixtures (the so-called triplet emitters) were proposed for the insertion into the emitting layer. In particular, these are metal porphyrins and organic heavy metal complexes [2–6, 11–13]. Owing to the strong spin-orbit interaction induced by a metal atom, the phosphorescence quantum yield Φ_{Ph} for those molecules considerably increases. For example, for the solid solution of bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}](acetylacetonate) iridium (Btp₂Ir(acac)) in 4,4'-bis(N-carbazolyl)-diphenyl, $\Phi_{\text{Ph}} = 0.51$ at room temperature [3]. As a basis of active layers, compounds were also proposed to be used [12], in which the excitation gives rise with a high probability to the intercombination conversion $S_1 \rightarrow T_1$ from the first excited singlet S_1 state into the triplet T_1 one, followed by the transfer of triplet excitons to the triplet emitter.

The aim of the work is to compare the efficiency of the electron excitation energy transfer by singlet and triplet excitons to the triplet emitter in poly-N-epoxypropylcarbazole (PEPC). Photophysical properties of this polymer are very close to those of poly-N-vinylcarbazole [14], which is often used as a basis for polymer light-emitting diodes [1, 2, 4–7]. For this purpose, we have measured the luminescence spectra for films of pure PEPC and its dihalogen derivatives poly-N-epoxypropyl-3,6-dichlorocarbazole (DCIPEPC) and poly-N-epoxypropyl-3,6-dibromocarbazole (DBrPEPC), and have deter-

mined Φ_{Fl} and Φ_{Ph} ; we have measured Φ_{Ph} for Btp₂Ir(acac) molecules in polystyrene (PS) films and films of carbazolyl-containing polymers. We have also studied the spectra of PEPC films with two admixtures: Btp₂Ir(acac) and benzophenone. The chemical formulas of the polymers and admixtures concerned are depicted in Fig. 1.

2. Experimental Technique

The PS polymer was obtained from BASF (Germany); the PEPC, DCIPEPC, and DBrPEPC polymers from the Institute of Electrophotography (Vilnius); Btp₂Ir(acac) from American Dye Source Inc. (USA); and benzophenone from Sigma-Aldrich. The polymers and admixtures were dissolved separately in tetrahydrofuran (to the polymer concentration $C = 5 \div 10$ wt.%), mixed, and held at room temperature for several hours. Films 20–30 μm in thickness were deposited by watering solutions on substrates fabricated from fused quartz. Afterward, the specimens were dried at room temperature.

Luminescence spectra were excited by applying the radiation of a high-pressure mercury lamp DRSh-250-3 through a glass absorption filter for the line group at $\lambda_{\text{exc}} = 313$ nm and measured on a spectrometer SDL-1. In low-temperature measurements, an optical helium cryostat with the automatic control and a temperature stabilization unit was used, which was developed and produced at the Institute of Physics of the NAS of Ukraine.

The absolute value of the fluorescence quantum yield Φ_{Fl} at $T = 295$ K was determined by comparing the integral fluorescence (FL) intensities of the specimen and the solution of Tri-p-tolylamine ($C = 10^{-5}$ M) in toluene, for which $\Phi_{\text{Fl}} \approx 0.045$ [15]. At the temperature $T = 5$ K, the value of Φ_{Fl} was obtained by comparing the integral fluorescence intensities of the specimen measured at $T = 295$ and

5 K. The Φ_{F1} and Φ_{Ph} values for DCIPEPC and DBrPEPC were determined with respect to the Φ_{F1} value obtained for the PEPC film at $T = 5$ K. The measurement accuracy amounted to $\pm 10\%$.

3. Experimental Results

It is well-known [16] that a $Btp_2Ir(acac)$ molecule phosphoresces owing to the radiative transition from the triplet ${}^3LC(btp-\pi\pi^*)/{}^3(MLCT-d\pi^*)$ state into the ground one. This triplet state was formed by mixing the ${}^3(btp-\pi\pi^*)$ state, which was centered at the (btp)-ligand (3LC state), and a state with charge transfer from the $5d$ orbital of an iridium atom to the ${}^3\pi^*$ orbital of the (btp)-ligand (3MLCT state). Owing to the strong spin-orbit coupling, the T_1 state induced by an iridium atom was mixed with singlet states located higher, and the probability of the intercombination conversion $S_1 \rightarrow T_1$ amounted to 100%, with the molecule only phosphorescing [16, 17].

At room temperature, the phosphorescence spectrum of the $Btp_2Ir(acac)$ solution in PS ($C = 3$ wt.%) consisted of three bands with maxima at $\lambda_{max} \approx 618$, 670, and 740 nm (Fig. 2, curve 1). If PS was substituted by PEPC or its dihalogen analogs, the positions of phosphorescence maxima did not change, but their intensities significantly decreased (Fig. 2, curves 2 to 4). The quantum yields amounted to $\Phi_{Ph} = 0.50$, 0.27, 0.08, and 0.05 in the cases of PS, PEPC, DCIPEPC, and DBrPEPC matrices, respectively.

The luminescence spectra of PEPC and its dihalogen-substituted analogs measured at $T = 5$ K are depicted in Fig. 3. In the spectrum of PEPC film, three photoluminescence bands can be distinguished at $\lambda_{max} \approx 360$, 375, and 390 nm, and a structured phosphorescence spectrum starting at $\lambda_{max} = 419$ nm (curve 1), which are associated with the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions, respectively, in the lateral carbazole groups [18]. When changing from PEPC to its dihalogen-substituted analogs, substantial modifications take place in the spectrum structure and its quantitative characteristics. In particular, the low-intensity photoluminescence of the DCIPEPC film included three bands with maxima at $\lambda_{max} \approx 380$, 395, and 415 nm; the DBrPEPC film did not fluoresce at all; and the structured phosphorescence spectra of those polymers began by bands at $\lambda_{max} \approx 450$ and 435 nm, respectively (curves 2

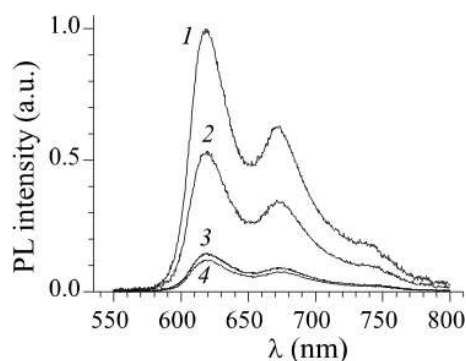


Fig. 2. Phosphorescence spectra of films of PS (1), PEPC (2), DCIPEPC (3), and DBrPEPC (4) with $Btp_2Ir(acac)$ (concentration $C = 3$ wt.%) measured under identical excitation and registration conditions: $T = 295$ K and $\lambda_{exc} = 313$ nm

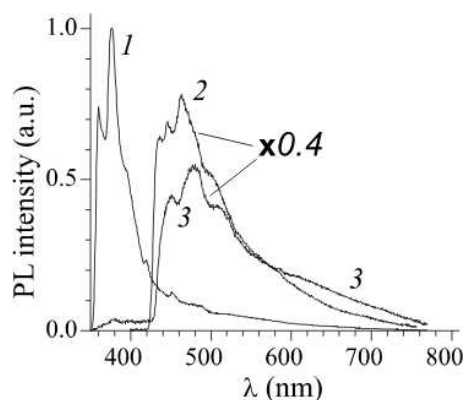


Fig. 3. Luminescence spectra of PEPC (1), DCIPEPC (2), and DBrPEPC (3) films measured under identical excitation and registration conditions: $T = 5$ K and $\lambda_{exc} = 313$ nm

and 3). Besides the structured spectrum, the films of PEPC and its dihalogen-substituted analogs demonstrated a wide unstructured phosphorescence band in the green spectral interval at $\lambda_{max} \approx 500$ nm. This band belongs to oxidation products, which are always available in carbazoyl-containing polymers [19, 20].

After introducing two chlorine atoms into lateral carbazoyl groups in PEPC, the quantum yield Φ_{F1} was 20 times lower, whereas the quantum yield Φ_{Ph} higher by almost the same factor. At the same time, after the chlorine atoms were substituted by bromine ones, Φ_{F1} vanished, whereas Φ_{Ph} increased by only 25% (Table 1). The indicated changes of Φ_{F1} and Φ_{Ph} are related to the probability growth for the intercombination transitions $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ under the influence of internal heavy halogen atoms [21].

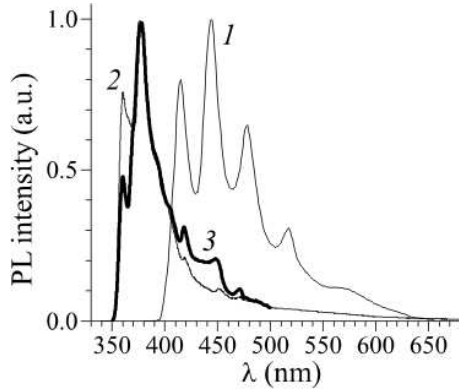


Fig. 4. Normalized luminescence spectra: benzophenone solution in PS (the concentration $C = 5$ wt.%) (1), pure PEPC film (2), and film of PEPC with the benzophenone admixture (the concentration $C = 5$ wt.%) (3). $T = 5$ K and $\lambda_{exc} = 313$ nm

When the temperature was increased to room one, Φ_{F1} decreased approximately twice as much, and Φ_{Ph} decreased to zero. Note that the data in Table 1 concerning the relative variation of Φ_{F1} along the series PEPC, DCIPEPC, and DBrPEPC are in a qualitative agreement with the literature data on the solutions of carbazole and its dihalogen-substituted analogs [22].

The PS polymer does not absorb light at $\lambda = 313$ nm. Therefore, the T_1 state of Btp₂Ir(acac) can be populated only due to the intercombination conversion $S_1 \rightarrow T_1$ after the direct photoexcitation of its molecules. In turn, the admixtures at the indicated concentration in the matrices of PEPC and its dihalogen-substituted analogs were mainly excited as a result of the energy transfer from the matrix [20]. The magnitude of the ratio between Φ_{Ph} of a Btp₂Ir(acac) molecule at its excitation through the matrix of the carbazolyl-containing polymer and Φ_{Ph} of this molecule in PS (i.e. at the direct excitation) can serve as an efficiency criterion for the energy transfer from the basis to the admixture.

Table 1. Quantum yields Φ_{F1} and Φ_{Ph} for films of pure PEPC, DCIPEPC, and DBrPEPC

Polymer	$T = 5$ K		$T = 295$ K
	Φ_{F1}	Φ_{Ph}	Φ_{F1}
PEPC	0.22	0.70×10^{-2}	0.11
DCIPEPC	0.01	0.12	0.007
DBrPEPC	0	0.15	0

The PEPC polymer both fluoresced and phosphoresced. Therefore, the excitation energy was transferred by both singlet and triplet excitons. On the contrary, the DBrPEPC polymer only phosphoresced, and, as was found in our previous works [20, 23], the excitation energy was transferred only by triplet excitons. The quantum yield Φ_{Ph} of a Btp₂Ir(acac) molecule in PEPC was five times as high as in DBrPEPC. Therefore, we may assume that the efficiency of the energy transfer in PEPC by singlet excitons is higher than by triplet ones. To prove this hypothesis directly, we compared the intensities of the sensitized phosphorescence by Btp₂Ir(acac) molecules in two matrices: pure PEPC and PEPC with the benzophenone admixture.

The luminescence spectra of benzophenone in PS, as well as films of pure PEPC and PEPC with the benzophenone admixture, which were measured at $T = 5$ K, are exhibited in Fig. 4. After the excitation of benzophenone in the PS matrix, the intercombination conversion $S_1 \rightarrow T_1$ took place with a probability of about 100% [21], so that the molecule only phosphoresced. The spectrum of this phosphorescence began by a band with $\lambda_{max} \approx 415$ nm (curve 1). Hence, in the PEPC matrix, the energy of benzophenone T_1 level is higher than the energy of PEPC T_1 level by about 230 cm^{-1} ($E_T \approx 24100$ and 23870 cm^{-1} , respectively). Since the distance between the S_1 and T_1 levels in benzophenone amounted to $E_{ST} \approx 1600 \text{ cm}^{-1}$ [21], the S_1 level of benzophenone is located below the S_1 level of PEPC by about 2100 cm^{-1} ($E_S \approx 25700$ and 27800 cm^{-1} , respectively). Therefore, the following processes are possible when exciting a PEPC film with the benzophenone admixture: 1) transfer of the singlet exciton energy to benzophenone, 2) intercombination conversion $S_1 \rightarrow T_1$ in the benzophenone molecule, and 3) transfer of the triplet excitation energy from benzophenone to the PEPC carbazolyl group. As a result of those processes, some singlet excitons transformed into triplet ones, which was evidenced by a growth in the relative intensity of the PEPC phosphorescence signal (Fig. 4, curves 2 and 3).

After the Btp₂Ir(acac) admixture was introduced into the PEPC film to the concentration $C = 0.1$ wt.%, the matrix fluorescence intensity became half as high, and the sensitized phosphorescence of a Btp₂Ir(acac) molecule appeared (Fig. 5, a, curves 1 and 2). In the case where two admixtures were

added to PEPC – Btp₂Ir(acac) to the concentration $C = 0.1$ wt.% and benzophenone to the concentration $C = 5$ wt.% – not only the matrix fluorescence intensity decreased by a factor of one and a half, but also the sensitized phosphorescence intensity of Btp₂Ir(acac) diminished almost twice (Fig. 5, *a*, curve 3). When the Btp₂Ir(acac) concentration was increased to $C = 3$ wt.%, the matrix fluorescence was completely extinguished, and only the sensitized fluorescence of Btp₂Ir(acac) was observed (Fig. 5, curves 1 and 2). The additional introduction of benzophenone to the concentration $C = 5$ wt.% resulted in a reduction of the Btp₂Ir(acac) sensitized fluorescence intensity by almost a factor of one and a half (Fig. 5, curve 3). Therefore, the Btp₂Ir(acac) sensitized fluorescence intensity considerably decreased after molecules of the benzophenone admixture transformed some singlet excitons in PEPC into triplet ones.

4. Discussion of Experimental Results

Hence, both the singlet-singlet and triplet-triplet transfers of the electron excitation energy took place, when an acceptor of singlet and triplet excitons was introduced into fluorescent and phosphorescent PEPC and DCIPEPC, and only the triplet-triplet one, when the acceptor was introduced into phosphorescent-only DBrPEPC. When the distance between the chromophores in the basis (donor) and admixture molecules (acceptor) several times exceeded the sum of their van der Waals radii, the radiationless energy transfer at dipole-allowed transitions took place owing to the resonance dipole-dipole interaction, i.e. following the Förster mechanism [24]. In this case, the molecular spin state was preserved, and only the singlet-singlet transfer was allowed. The rate constant of the energy transfer process k_{DA} depended on the distance R_{DA} between the donor and the acceptor, the transfer critical radius R_0 , and the donor fluorescence decay time in the acceptor absence, τ_D :

$$k_{DA} = (\tau_D)^{-1} (R_0/R_{DA})^6. \quad (1)$$

The value of the parameter R_0 was given by the expression [17, 25]

$$R_0^6 = \frac{9000\chi^2 \ln 10}{128\pi^5 N_0 n^4} \Phi_D \int F_D(\nu) \frac{d\nu}{\nu^4}. \quad (2)$$

Here, χ^2 is the orientational factor ($\chi^2 = 2/3$ for the randomly oriented donor and acceptor), N_0

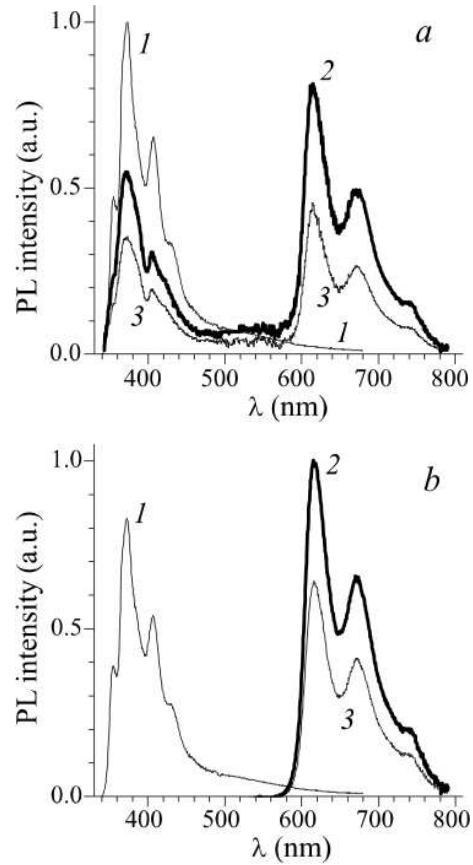


Fig. 5. Luminescence spectra of films of pure PEPC (1), PEPC with the Btp₂Ir(acac) admixture (2), and PEPC with the Btp₂Ir(acac) and benzophenone admixtures measured under identical excitation and registration conditions (3): $T = 295$ K and $\lambda_{exc} = 313$ nm. Concentration of benzophenone $C = 5$ wt.%. Concentrations of Btp₂Ir(acac) $C = 0.1$ (a) and 3 wt.% (b)

the Avogadro constant; Φ_D the donor fluorescence quantum yield, n the refractive index of the basis (for carbazoly- containing polymers, $n \approx 1.62$ [26]), $F_D(\nu)$ the normalized donor fluorescence spectrum (i.e. $\int F_D(\nu) d\nu = 1$), $\epsilon_A(\nu)$ the acceptor molar extinction coefficient, and ν the wave number. On the basis of the data available for the absorption by Btp₂Ir(acac) [17] and polymer fluorescence, it was found that, at room temperature, $R_0 \approx 2.3$ and 1.0 nm for PEPC and DCIPEPC, respectively.

The Förster mechanism is efficient in the case $R_{DA} \leq R_0$. If the acceptor molecules are distributed uniformly (this fact was proved for Btp₂Ir(acac) molecules [17]), every of them is surrounded by an

imaginary sphere, and if the concentration C is measured in mole units, the radius of this sphere (in nanometers) amounts to [20]

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

For the concentration $C = 0.1 \div 3$ wt.%, i.e. $C = (0.14 \div 4.23) \times 10^{-2}$ M, we obtain $R_{\text{DA}} = 2.1 \div 6.6$ nm, and the distance between the donor and the acceptor can exceed R_0 . Therefore, the energy of a singlet exciton was transferred in two stages: at first, excitons migrated, and when the distance to the acceptor diminished to R_0 , the energy was transferred to the acceptor with a probability of 50%.

If the donor and acceptor molecules approached each other so that their molecular orbitals became partially overlapped, the electron exchange interaction prevailed, and the energy transfer was described by the Dexter theory [24]. In this case, the total spin of the system was preserved, and both the singlet-singlet and triplet-triplet transfers were allowed (at a distance to 1.0–1.5 nm).

Since the polymers examined 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. For a jump into a state with a higher energy, the activation energy is required. In the Bassler model [25, 27], it is supposed that the density distributions for the energy states of singlet and triplet excitons (DOS_S and DOS_T , respectively) in disordered systems are described by Gaussian functions:

$$\text{DOS}_S \sim \exp[-(\nu_S - \nu)^2 / (2\sigma_S^2)], \quad (4)$$

$$\text{DOS}_T \sim \exp[-(\nu_T - \nu)^2 / (2\sigma_T^2)], \quad (5)$$

where ν_S and ν_T are the Gaussian centers, and σ_S and σ_T the Gaussian half-widths.

Table 2. Parameters σ_S and σ_T for PEPC, DCIPEPC, and DBrPEPC films

Polymer	σ_S, cm^{-1}	σ_T, cm^{-1}
PEPC	330	250
DCIPEPC	500	400
DBrPEPC	–	230

Calculations using the Monte Carlo method showed [27] that, at low temperatures ($\sigma_S \gg kT$ and $\sigma_T \gg kT$, where k is the Boltzmann constant), excitons executed several jumps and became localized in the tail states. The corresponding density distribution functions for the occupied states also acquired the Gaussian form with the half-widths σ_S and σ_T equal to the half-widths of the functions DOS_S and DOS_T , respectively. This circumstance allowed us to determine σ_S and σ_T by applying the Gaussian functions (4) and (5) to approximate the short-wave wing of the initial band in the fluorescence and phosphorescence spectra of PEPC, DCIPEPC, and DBrPEPC films, which were measured at $T = 5$ K. The results of approximation are quoted in Table 2. As follows from the presented data, $\sigma_S > kT$ and $\sigma_T > kT$ at room temperature ($kT \approx 210 \text{ cm}^{-1}$), and no equilibrium between excitons and phonons was established [27]. As a result, during the migration, some excitons were localized in the tail states and did not participate in the further energy transfer. Therefore, when the PS matrix was substituted by the carbazoyl-containing polymer, the Φ_{Ph} -value for the Btp₂Ir(acac) admixture decreased.

In PEPC, in the case of energy transfer to Btp₂Ir(acac) by a singlet exciton and provided that $R_{\text{DA}} > R_0$, the exciton, owing to the migration, passed only some part of the distance. When R_{DA} diminished to R_0 , the energy was transferred to the acceptor with a probability of 50%. At the same time, at the energy transfer by means of the electron short-range exchange interaction, a triplet exciton should pass the whole distance to the acceptor following the migration mechanism. Carbazoyl-containing polymers are known to always contain oxidates, which form deep traps for triplet excitons [19, 20]. The probabilities of the exciton localization in the tail states and the exciton capture by deep traps increase as the migration path length grows. Therefore, the efficiency of the energy transfer by triplet excitons is lower than by singlet ones.

Unlike DBrPEPC, DCIPEPC fluoresced (Fig. 3, curves 2 and 3), and the excitation energy was transferred to Btp₂Ir(acac) by not only triplet but also singlet excitons. Therefore, the quantum yield Φ_{Ph} of sensitized phosphorescence of Btp₂Ir(acac) molecules in the DCIPEPC matrix is higher than in the DBrPEPC one. At the same time, the value of R_0 for Btp₂Ir(acac) in the DCIPEPC matrix is more than

twice less than in PEPC. Therefore, at the energy transfer by the migration, singlet excitons passed a larger, on average, distance than in the PEPC matrix, and the quantum yield Φ_{PH} of the sensitized phosphorescence of Btp₂Ir(acac) molecules in DCIPEPC was lower than in PEPC.

In contrast to the results obtained in this work, the authors of work [28] found that, for typical molecular crystals, such as durol and diphenyl, the efficiency of the energy transfer by triplet excitons at room temperature is at least 10 times higher than by singlet excitons. We explain this distinction as follows. First, unlike the carbazoly-containing polymers researched in this work, molecular crystals have an ordered structure, and the energy states of excitons form bands in them. Owing to a very weak intermolecular interaction, the bands of triplet excitons are very narrow (their width varies from a few to several tens of inverse centimeters [29]), and excitons actually migrate between “isoenergetic” states. Second, the concentration of uncontrollable admixtures in highly purified molecular crystals is much lower than in carbazoly-containing polymers.

5. Conclusions

To summarize, it is found that the quantum yield of the sensitized phosphorescence of Btp₂Ir(acac) molecules in the PEPC matrix is half as high as at their direct excitation in the PS matrix, but more than three and five times as high as in DCIPEPC and DBrPEPC, respectively. After the second impurity, benzophenone, was additionally introduced into PEPC with the Btp₂Ir(acac) admixture, it transformed some singlet excitons into triplet ones, and the intensity of the sensitized phosphorescence of Btp₂Ir(acac) also decreased. In PEPC, which both fluoresced and phosphoresced, the excitation energy was transferred by both singlet excitons (by means of the migration and long-range dipole-dipole interaction) and triplet ones (by means of the migration and short-range electron exchange interaction). In DBrPEPC, which only phosphoresced, the excitation energy was only transferred by triplet excitons. From the analysis of the luminescence spectra of pure films, it is found that, during the migration, some singlet and triplet excitons became localized in the tail energy states. Moreover, the indicated polymers contained uncontrollable admixtures,

namely, oxidates, which form deep traps for triplet excitons. Therefore, the quantum yield of the sensitized phosphorescence of Btp₂Ir(acac) molecules in the carbazoly-containing polymers is lower than that obtained at their direct excitation in the PS matrix, with the efficiency of the excitation energy transfer by singlet excitons being higher than by triplet ones. Therefore, the PEPC polymer is more suitable for the practical application in optoelectronic devices than its dihalogen-substituted analogs.

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ПОРІВНЮВАННЯ ЕФЕКТИВНОСТЕЙ
ПЕРЕНОСУ ЕНЕРГІЇ ЗБУДЖЕННЯ СИНГЛЕТНИМИ
І ТРИПЛЕТНИМИ ЕКСИТОНАМИ
В КАРБАЗОЛІВМІСНИХ ПОЛІМЕРАХ

Резюме

Досліджені спектри люмінесценції чистих плівок полі-N-епоксипропілкарбазолу (РЕРС), полі-N-епоксипропіл-3,6-діхлоркарбазолу (ДСІРЕРС) і полі-N-епоксипропіл-3,6-дібромкарбазолу (ДВrРЕРС) та з домішкою біс[2-(2'-бензотієніл)-піридинаго-N,C^{3'}](ацетилацетонату) іридію (Vtr₂Ir(acac)), плівок полістиролу (PS) з домішкою Vtr₂Ir(acac), а також плівок РЕРС з двома домішками – бензофенону і Vtr₂Ir(acac). Зазначені полімери перспективні для практичного використання в оптоелектронних пристроях. Визначено, що у РЕРС енергія збудження переносилася як синглетними екситонами шляхом міграції і далекодіючої диполь-дипольної взаємодії, так і триплетними через міграцію і короткодіючу обмінну електронну взаємодію, а у випадку ДВrРЕРС, який лише фосфоресцював – тільки триплетними екситонами. Встановлено, що квантовий вихід сенсibilізованої фосфоресценції молекул Vtr₂Ir(acac) в матриці карбазолівмісного полімеру нижчий, ніж при прямому їх збудженні в матриці PS, при цьому в РЕРС він був, відповідно, у три і п'ять разів вище, ніж у ДСІРЕРС і ДВrРЕРС. Показано, що після трансформації молекулами бензофенону частини синглетних екситонів РЕРС у триплетні, інтенсивність сенсibilізованої фосфоресценції Vtr₂Ir(acac) зменшувалась. Зроблено висновок про те, що в процесі міграції частина синглетних і триплетних екситонів локалізувалася в хвостових енергетичних станах, і, крім того, частина триплетних екситонів захоплювалася продуктами окислення полімеру.