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# PECULIARITIES OF ELECTRONIC PROCESSES IN HIGH-FLUORESCENCE BORON-CONTAINING COMPOSITE FILMS

*The absorption and fluorescence spectra of new boron-containing dyes in pure thin films of these dyes, as well as in double-components films of the "matrix–dye (impurity)" type, are studied. As matrix materials, tris(8-hydroxyquinolinato)aluminum (Alq3) and 3,6-di(9-carbazolyl)-9-(2-ethylhexyl) carbazole (Tcz1) are used. The thin films were obtained by the method of vacuum deposition. The comparison of the absorption spectra of the dyes in solutions and films shows that the destruction of dye molecules is not observed in the process of vacuum deposition. For double-component films, the electronic excitation energy transfer from matrix molecules to dye molecules is established. The optimum concentration of dyes for the light-emitting layers of organic light-emitting diodes (OLEDs) based on these compounds is determined.*

*Keywords:* cyanine dyes, vacuum deposition, thin films, OLED, boron-containing complexes.

## 1. Introduction

More than 19% of produced electricity in developed countries are known to be used for lighting purposes [1]. One way to reduce the energy costs of light sources is the use of a new class of devices such as white organic light-emitting diodes (WOLED) due to their high energy efficiency, low weight, flexibility, and low-cost manufacture [2, 3]. They can also be used in solid-state lighting sources for new color displays, as a backlight in LCD monitors [4–6]. The main component of WOLED, which determines the spectral characteristics of its radiation, is the light-emitting layer. The development of new materials for light-emitting layers with high-efficiency photo- and electroluminescence and the search for the new opportunities of management of color radiation are promising [7–10].

In this paper, we study specially designed molecules of cyanine dyes with high fluorescence quantum yields in the solid solutions. In these substances, the low probability of nonradiative transitions is achieved by introducing boron-containing groups, which increase the rigidity of the molecular frame [11]. The use of such substances as impurities makes it possible to control the color electroluminescent emission layer, due to the transfer of the excitation energy from the matrix molecules to the molecules of impurities, with the further fluorescence of impurity molecules. The process of electronic excitation energy transfer in the "matrix–impurity" system can efficiently occur if the matrix luminescence spectrum overlaps with the absorption spectrum of impurities. In this pa-

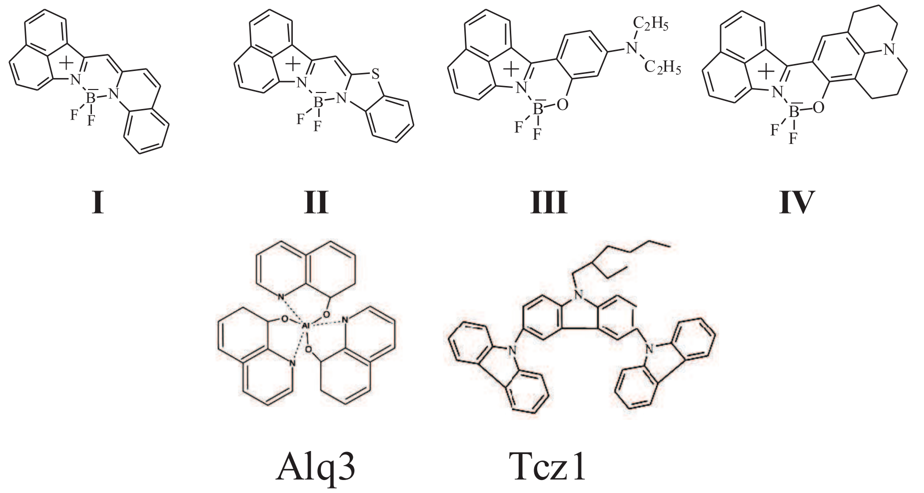

***Fig. 1.*** Chemical formulas of impurity emitting centers of dyes (I, II, III, IV) and matrices (*Alq*3, *Tcz*1)

per, the photophysical properties of composite films of the "matrix–impurity" system with matrices *Alq*3 and *Tcz*1 and the impurities of new boron-containing dyes I, II, III, and IV (Fig. 1) are investigated.

## 2. Experimental Section

The structure formula of new boron-containing dyes I, II, III, IV and *Alq*3, *Tcz*1 matrices are presented on Fig. 1. These dyes were synthesized in the Institute of Organic Chemistry (National Academy of Sciences of Ukraine) in the department of color and structure of organic compounds. The synthesis of these dyes was described in [12] in detail. Thin films were created on the base of a vacuum chamber UVN-74, using the standard vacuum deposition technique which is described in [13] in detail. The powders of investigated substances were deposited on glass and quartz substrates which were chemically cleaned in dimethylformamide and monoethanolamine under a pressure of $8 \times 10^{-6}$ Torr. The growth velocity of thin films and the dye concentration were controlled *in situ*, using the water cooling quartz sensors and the software Sigma SQM 242. The film thicknesses were measured by atom force microscopy and were in the interval 200–300 nm. The substrate temperature was not greater than 40 °C that excluded the evaporation of the film substance and destroying the film structure. The fluorescence spectra were registered on a spectrofluorometer Carry Eclipse (Varian), and the absorption spectra were registered on a Specord UV Vis. For the investigation of photophysical properties of dyes in solution, the tetrahydrofuran as a solvent was used. All fluorescence and absorption spectra were recorded at room temperature, $T = 293$ K.

## 3. Results and Discussion

The main part of OLED is the light emitting layer which is the one or many-component efficient electroluminescent thin film. One of the most efficient and cheap techniques for the thin film fabrication is the vacuum deposition. But one of the possible disadvantages of this method is the destruction of intermolecular bonds of dye molecules onto separate fragments during the evaporation [13]. So, for the testing of the dye abilities to be deposited in vacuum, the series of composite thin film samples (system "dye + matrix") were created, using the vacuum deposition technique. Each composite thin film consists of the matrix substance (*Alq*3 and *Tcz*1) and contains one dye (I, II, III, IV) as an impurity.

The absorption spectra of these composite thin films are compared with the dye absorption spectra in a tetrahydrofuran solution (see Fig. 2). For all absorption spectra of composite thin films, a small shift and a broadening of the absorption maxima are observed in comparison with the absorption maxima in solution.

But, in general, the dye absorption spectra have the similar shapes and structures in liquid tetrahydrofuran and solid solutions. This similarity proves

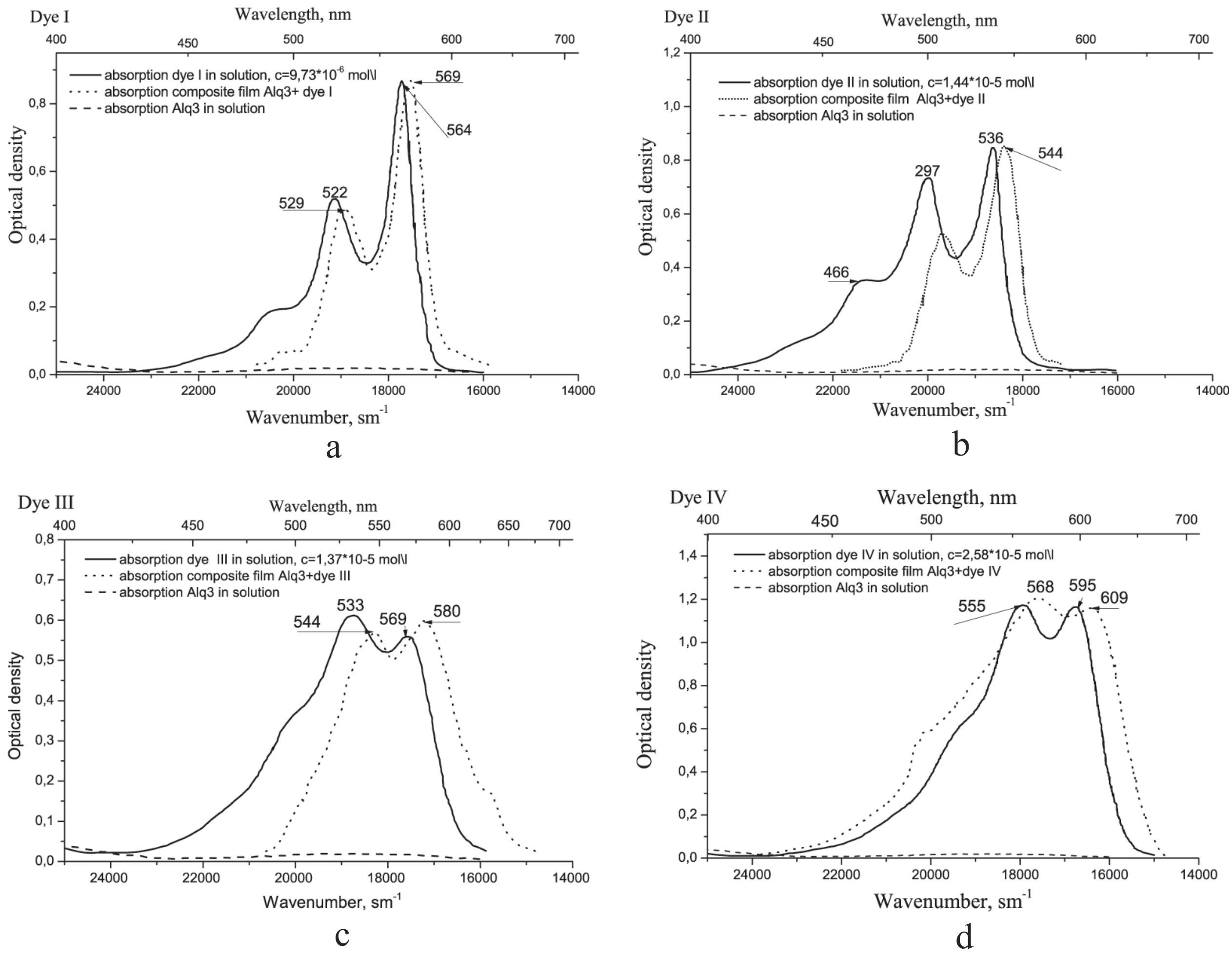

***Fig. 2.*** Absorption spectra of dyes I, II, III, and IV in a tetrahydrofuran solution (solid line) and those of composite "matrix–impurity" thin films (dotted line)

that the thin films are formed by dye molecules or their fragments, but not by the products of molecular destruction. molecular destruction. Second, the interaction between neighboring molecules in solid thin films is small, and the molecules absorb and emit as separate centers, as in case of liquid solutions. The spectral manifestations of intermolecular interactions in the investigated thin films appear in a small asymmetry of lower vibrational states in the absorption and fluorescence spectral bands and in a small shift of the absorption and fluorescence spectra of solid thin films in comparison with the corresponding spectra in liquid solutions. So, we can conclude that the vacuum deposition technique can be used for the thin film fabrication of investigated dyes without destroying their molecular

It is well known that photoluminescence and electroluminescence spectra have the same properties, so the next step was to investigate the photophysical properties of composite thin films (system "matrix–dye-impurity"), where the excitation can be transferred from matrix molecules to dye molecules, which are the main light-emitting centers in films [14]. The composite thin films contain two components: matrix and dye-impurity. The fluorescence spectra of composite thin films (system "matrix + dye impurity") and the corresponding fluorescence spectra of dyes in tetrahydrofuran solution are depicted on Fig. 3. The dye fluorescence spectra in both cases are very sim-

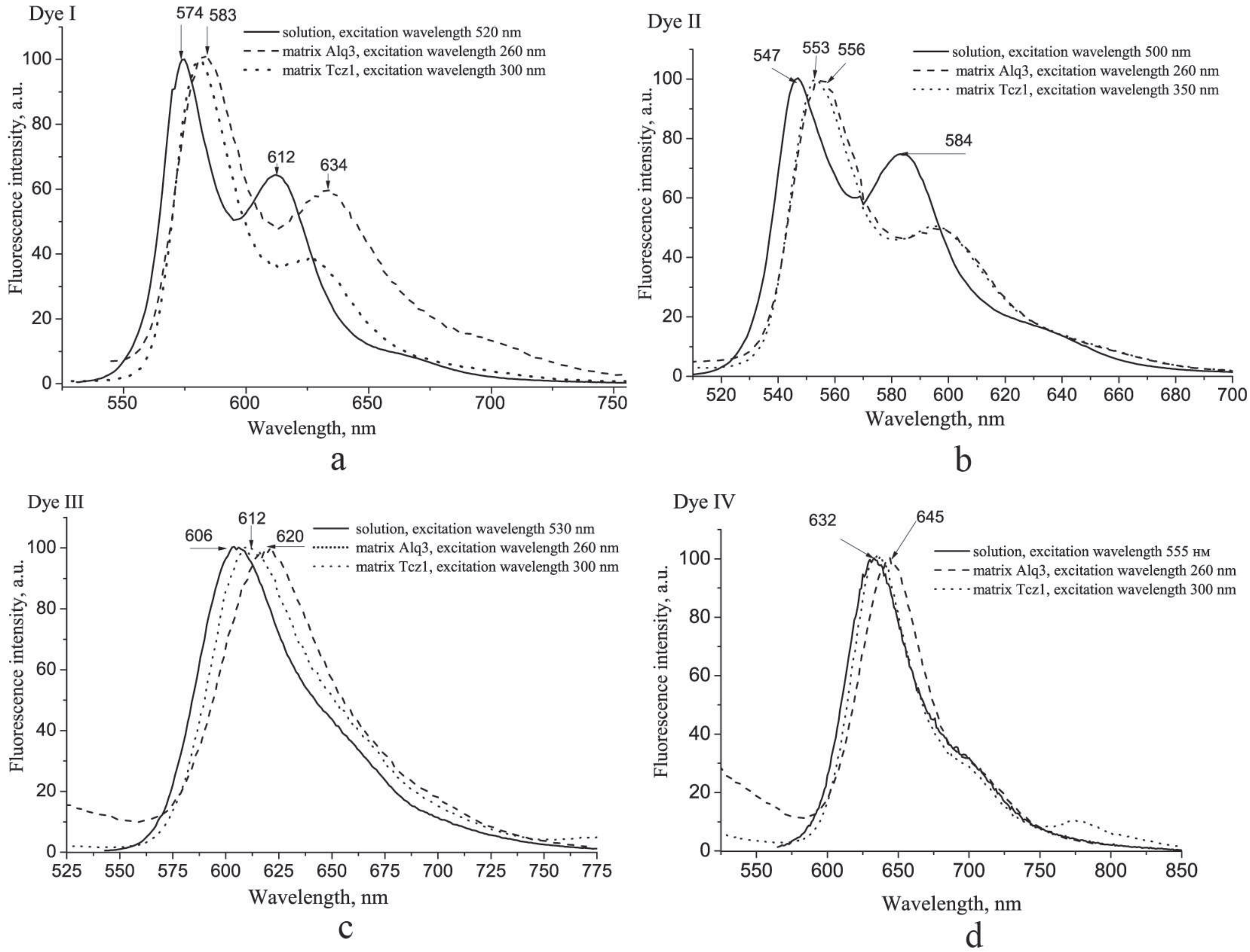

***Fig. 3.*** Fluorescence spectra of the dyes in a tetrahydrofuran solution (solid line), the matrix *Alq*3 (dotted line), and the matrix *Tcz*1 (dotted line). For each spectrum, the excitation wavelength is indicated. All spectra were recorded at the room temperature $T = 293$ K

ilar. So, in solid liquid solutions, the dye molecules emit light as separate centers. The small centers. The small differences in fluorescence maximum peak liquid solutions can be associated with different influences of the intermolecular environments, for example, with different intermolecular interactions in a liquid solution and thin films. In solution and thin films. In Fig. 4, the absorption spectra of spectra of composite thin films, and composite thin film excitation spectra for each dye are depicted. It is clearly seen that depicted. It is clearly seen that the fluorescence excitation sample have shape close to that of the matrix absorption spectrum in the short-wavelength spectral range. The intensity of fluorescence spectral range. The intensity of fluorescence excitation spectra in the matrix absorption spectral range is much larger than that in the dye absorption spectral range (see Fig. 4). It should be noted that the *Alq*3 extinction coefficient near 260 nm is equal to $5 \times 10^5$ l/(mol·cm) [15], and the extinction coefficient near 260 nm for each dye is approximately equal to $2 \times 10^5$ l/(mol·cm). This is the evidence that the most part of incoming photons is absorbed by matrix molecules, but the most part of outgoing photons are emitted by dye molecules.

Unfortunately, it is very difficult to control the dye concentration in solid matrices and their homogeneous distribution in the whole volume of a thin film in the vacuum deposition technique. These disadvantages are linked with a lag of the evaporation and the

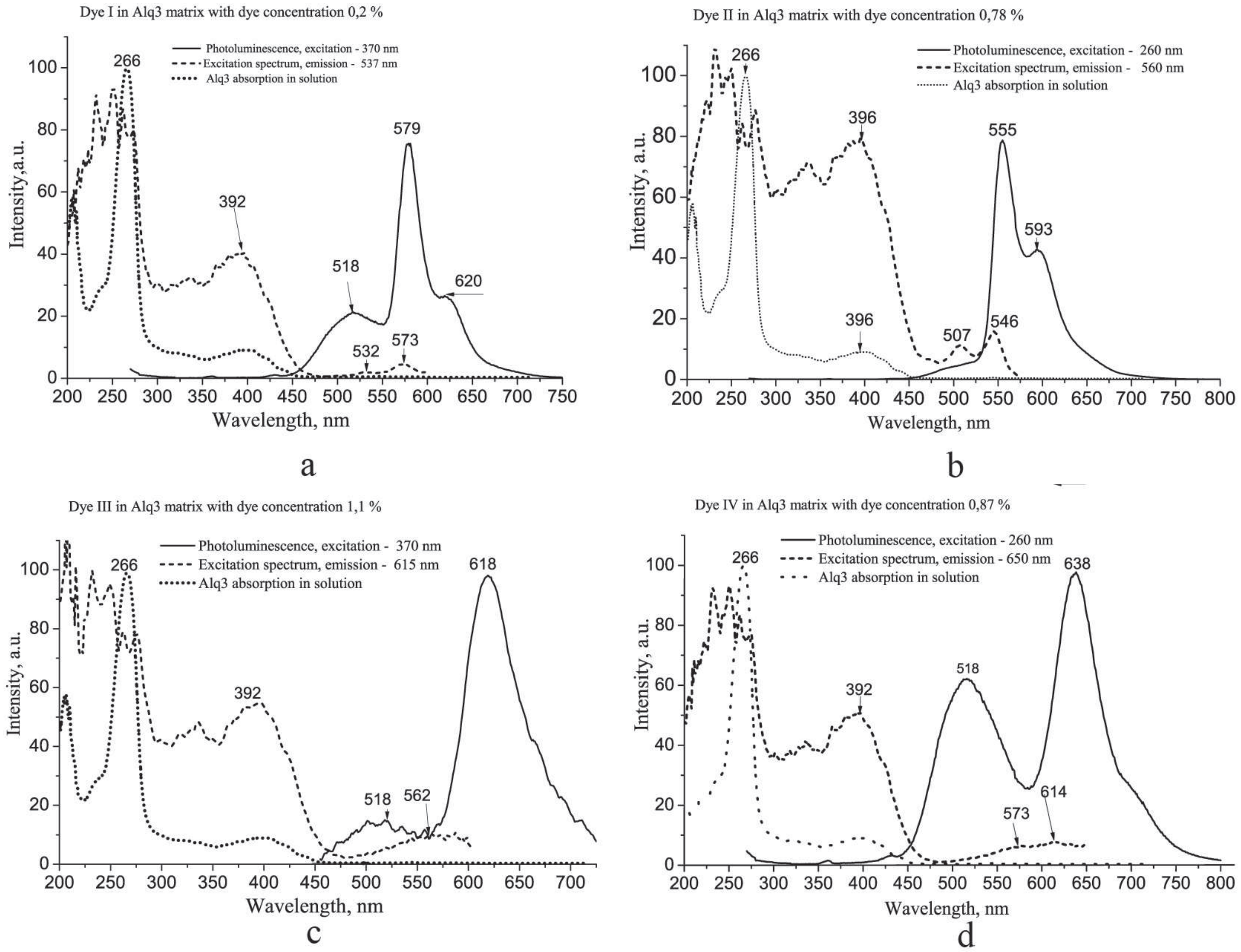

***Fig. 4.*** Absorption spectra of the *Alq*3 matrix in a tetrahydrofuran solution (dotted line), excitation spectra of composite thin films "dye – *Alq*3 matrix" (dashed line), and photoluminescence spectra of composite "dye – *Alq*3 matrix" thin films (solid line). All spectra were recorded at the room temperature $T = 293$ K. The dye impurity concentrations in the *Alq*3 matrix are shown for each dye

inhomogeneity of a vapor flow. Due to these reasons, the sequences of different samples with two matrices (*Alq*3 and *Tcz*1) were produced for seeking the optimal dye concentration. The fluorescence spectra of such composite systems are shown in Figs. 4 and 5. For comparison, the absorption and fluorescence spectra of pure matrix thin films are shown in Fig. 6.

At certain concentrations of impurities, the fluorescence intensity in the self-radiation range of dye molecules had a substantially large value in comparison with that in the intrinsic fluorescence range of the matrix. So, when the thin films are irradiated by exciting light, the excitation transfer process occurs between excited matrix molecules and non-excited dye molecules with the subsequent dominant dye fluorescence. The photoluminescence spectra of all composite thin films were recorded at room temperature, using the excitation wavelengths that correspond to the maxima of the absorption extinction coefficient in the spectral range of the intrinsic absorption for each matrix: 370 nm for *Alq*3, and 350 nm for *Tcz*1. The fluorescence spectra of the same samples which were recorded at different times are identical. This fact proves that the investigated dyes are photo-stable materials and, as a result, perspective materials for the fabrication of OLED layers.

For compound I in matrices *Alq*3 and *Tcz*1, the drastic increase in the dye fluorescence intensity in

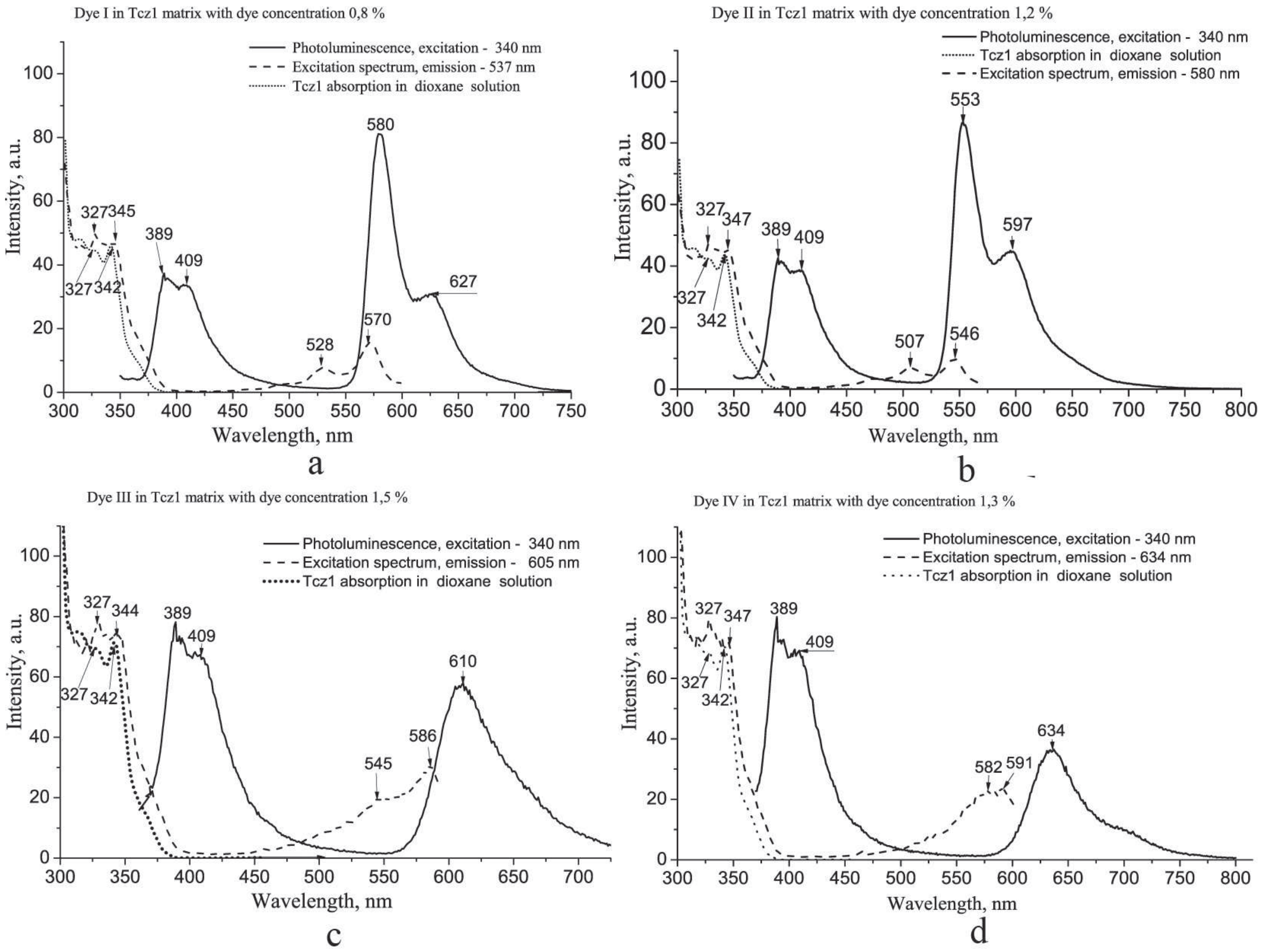

***Fig. 5.*** Absorption spectra of the $Tcz1$ matrix in a dioxane solution (dotted line), excitation spectra of composite "dye – $Tcz1$ matrix" thin films (dashed line), and photoluminescence spectra of composite "dye – $Tcz1$ matrix" thin films (solid line). All spectra were recorded at the room temperature $T = 293$ K. The dye impurity concentrations in the $Tcz1$ matrix are shown for each dye

comparison with the matrix fluorescence intensity was observed, when the dye concentration was 0.2% in the $Alq3$ matrix and 0.8% in the $Tcz1$ matrix (see Figs. 4, *a* and 5, *a*). The fluorescence excitation wavelengths were equal to 370 nm for $Alq3$ and 350 nm for $Tcz1$, which correspond to the absorption maxima for the corresponding matrices. For the $Alq3$ thin film fluorescence spectra, it is possible to detect the spectral peak near 422 nm, which is linked up with the fluorescence of $Alq3$ molecules. The intense peaks at 585 and 633 nm correspond to the dye fluorescence. The small shifts of the maximum positions in the composite film fluorescence spectra (shift for $Alq3$ – I film is equal to 48 nm, 585 nm in a solution, and 633 nm in a thin film; shift for $Tcz1$ – I matrix is equal to 38 nm, 585 nm in a solution, and 623 in a solid film) can be explained by different intermolecular interactions between dye and matrix molecules in different matrices.

In the case of the "matrix–compound II" system, the fluorescence was excited at light wavelengths of 260 nm and 300 nm for the $Alq3$ and $Tcz1$ matrices, respectively. The most intense dye fluorescence with the practically absent matrix fluorescence was fixed in the case of the $Alq3$ – II system with peaks at 556 and 596 nm, when the dye concentration was equal to 0.78% (see Fig. 4, *b*). For the $Tcz1$ – II system, we observed the intense dye fluorescence near 555 and

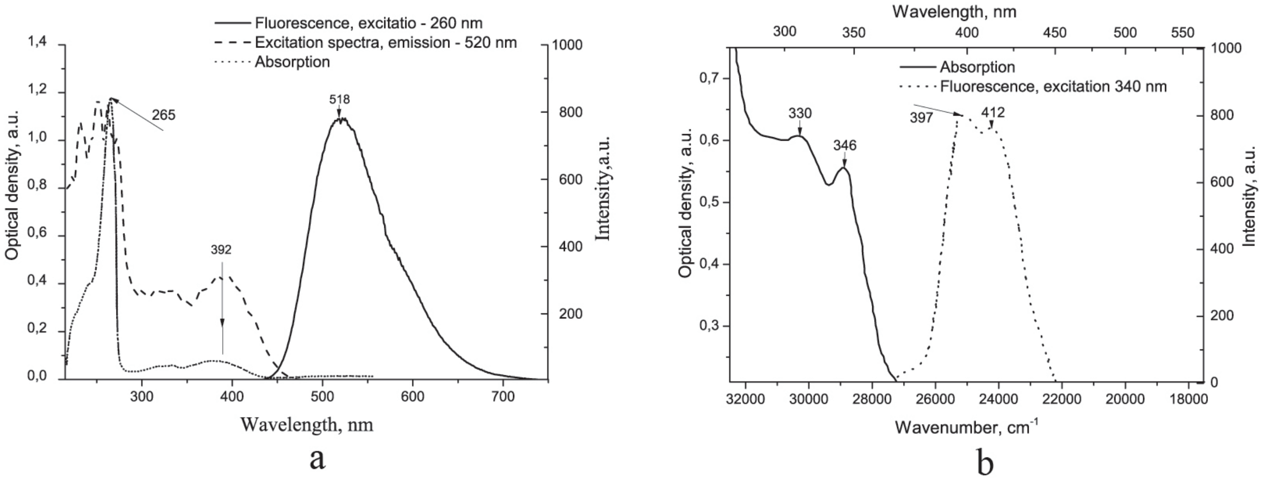

***Fig. 6.*** Fluorescence and absorption spectra of *Alq*3 (*a*) and *Tcz*1 [16] (*b*) matrix films

600 nm and the large quenching of the matrix fluorescence when the dye concentration was equal approximately to 1.2% (see Fig. 5, *b*).

For the "matrix–compound III" system, the fluorescence excitation wavelengths were 260 nm for the *Alq*3 matrix and 300 nm for the *Tcz*1 one, which correspond to the absorption maxima of the corresponding matrices. For the "*Alq*3 – dye III" system, the almost full absence of matrix fluorescence was observed (only very weak peak at 513 nm). For this film, the very strong dye fluorescence was observed especially near 628 nm for a dye concentration of 1.1% (see Fig. 4, *c*). For the "*Tcz*1 – dye III" system, a less efficiency of the electronic excitation transfer (practically equal intensity of matrix fluorescence-peaks at 392 nm and 400 nm, and dye fluorescence – peak at 611 nm) was observed. For the "*Tcz*1 – dye III" system, the strong matrix fluorescence (peak at 401 nm) and the weak dye fluorescence (peak near 630 nm at the 1.5-% dye concentration) were observed (see Fig. 5, *c*). The fluorescence of "matrix–compound IV" films was excited, using the excitation light with wavelengths of 260 nm for the *Alq*3 matrix and 300 nm for the *Tcz*1 one. The dye fluorescence was observed for *Alq*3 – IV system (peak near 658 nm). The matrix fluorescence was much weaker near 514 nm. The dye concentration in this case was equal to 0.87% (see Fig. 4, *d*). For the "*Tcz*1 – dye IV" system, we observed the strong matrix fluorescence (peaks at 388 and 410 nm) and the weaker dye fluorescence (approximately two-third of the matrix fluorescence intensity) near 643 and 710 nm (see Fig. 5, S*d*), when the dye concentration was equal to 1.3%.

Preliminary results suggest that the electronic excitation transfer between matrix and dye molecules should exist. The next stage of the research was the determination of such dye concentration in matrices, when the fluorescence dye intensity gained the maximum, and the excitation energy transfer became most efficient. For such purposes, the series of composite thin films were produced with different dye concentrations in samples. In these experiments, the *Alq*3 matrix was used. After that, we selected the samples, where the maximal dye fluorescence intensity was observed. Using the absorption spectra of selected samples, the dye concentration was determined. We obtained the following values for the relative concentrations of different dyes in the *Alq*3 matrix: for dye I – 1.1%, for dye II – 0.9%, for dye III – 1.1%, and for dye IV – 0.9%. With a further increase in the impurity concentrations in the matrix, a decrease in the fluorescence intensity of the composite film was observed. The possible reason for this is the nonradiative excitation transfer between excited molecules and nonfluorescent aggregates (aggregation clusters). At smaller values of the indicated concentrations, the process of excitation trapping by aggregates was not dominant.

## 4. Conclusion

The photophysical properties of the promising new materials, namely the new boron-containing dyes I,

II, III, and IV, have been investigated. The possibility of using the method of thermal deposition in vacuum for the production of the thin films of these materials is shown. The series of thin films of these dyes and the series of composite thin films with the $Tcz1$ and $Alq3$ matrices and with impurities of these dyes were fabricated. The increase of the fluorescence intensity of dyes with their concentration and the fluorescence quenching of the matrix in a certain range of dye concentrations in $Tcz1$ and $Alq3$ are established. The optimal concentrations of dyes in composite films are evaluated. For these concentrations, the composite films "$Alq3$ – dye" can be used as light-emitting layers in OLED. Multicomponent composite films of $Alq3$ with the addition of all four dyes can be used to fabricate white OLEDs.

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## ОСОБЛИВОСТІ ЕЛЕКТРОННИХ ПРОЦЕСІВ У ВИСОКОФЛЮОРЕСЦЕНТНИХ БОРМІСТКИХ КОМПОЗИТНИХ ПЛІВКАХ

### Резюме

Вивчено спектри поглинання і флюоресценції нових бормістких барвників в двокомпонентних плівках типу "матриця–барвник (домішка)". В ролі матеріалів матриці використовувались такі речовини, як тріс(8-хінолінол)алюміній ($Alq3$) і 3,6-ді(9-карбозоліл)-9-(2-етилгексіл) карбозол ($Tcz1$). Тонкі плівки було отримано методом вакуумного нанесення. Порівнюючи спектри поглинання барвників в розчині та в плівках встановлено, що в процесі вакуумного нанесення не спостерігається деструкція молекул барвників. Для двокомпонентних плівок встановлено факт перенесення енергії електронного збудження від молекул матриці до молекул барвників. Визначено оптимальні концентрації барвників для світловипромінюючих шарів органічних світлодіодів, що базуються на даних сполуках.