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Valeriy M. Yashchuk [a], Juozas V. Grazulevicius [b], Vitaliy V. Kosach [a], Jurate Simokaitiene [b], Kostyantyn M. Kushnir [a], Yurij T. Kononenko [a] & Antonina P. Naumenko [a]

[a] Physics Faculty, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

[b] Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania

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Spectral Properties of Carbazole- and Phenothiazine-Containing Low-Molecular Compounds for Photonics

VALERIY M. YASHCHUK,[1] JUOZAS V. GRAZULEVICIUS,[2] VITALIY V. KOSACH,[1] JURATE SIMOKAITIENE,[2] KOSTYANTYN M. KUSHNIR,[1] YURIJ T. KONONENKO,[1] AND ANTONINA P. NAUMENKO[1]

[1]Physics Faculty, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[2]Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania

Aza-compounds derivatives such as carbazole and phenothiazine are intensively studied as potential components of organic electronics, particularly of OLEDs. The present paper deals with investigations of spectral properties of specific carbazole- and phenothiazine-containing low-molecular glass-forming compounds, i.e., 3-(9-carbazolyl)-9-ethylcarbazole, 3-(9-pheothiazinyl)-9-ethylphenothiazine, 3-(9-pheothiazinyl)-9-ethylcarbazole, and 3-(9-carbazolyl)-9-ethylphenothiazine in different aggregative states (solid samples and solutions) and at different temperatures (77° K, 293° K). The location of the first singlet and triplet energy levels of the investigated compounds has been estimated from the spectral data. The high probability of the intercombinatory transition to the triplet state for the solutions and solid samples of 3-(9-pheothiazinyl)-9-ethylphenothiazine, 3-(9-pheothiazinyl)-9-ethylcarbazole, and 3-(9-carbazolyl)-9-ethylphenothiazine has been stated.

Keywords Carbazole; luminescence; organic glass-forming compounds; phenothiazine; singlet-triplet conversion

1. Introduction

The last decades are marked by the flurry of research work in the area of alternative energy sources, particularly of low-power inputs (energy saving) light sources. This stimulates the investigations of materials which could be used as an active medium in photo-electric cells (solar cells) and high efficient electroluminescent devices (the so-called LEDs, OLEDs, OPhEDs, etc.).

Address correspondence to Valeriy M. Yashchuk, Physics Faculty, Taras Shevchenko National University of Kyiv, 6, Acad. Glushkov Ave., Kyiv 03022, Ukraine. E-mail: vmyashchuk@mail.univ.kiev.ua

In this context, a more and more attention is paid to the organic materials which have a number of advantages over inorganic ones in the field of the development of electroluminescent systems and photo-electric cells. Some of these advantages are as follows: a possibility to create devices with large active area (m^2) using the simple printing or spin-coating technologies including such devices on the flexible base, high contrast and true black color of the organic displays, lower work voltage of the OLED diodes comparatively to the inorganic analogs, and so on. These reasons cause the rapid progress in investigations and the development of organic materials and nowadays continue to spark a huge amount of research.

When we point to such advantages of the organic compounds as the flexibility and a possibility to create luminescent devices with the large size active medium, this concerns polymers, first of all. However, the use of low-molecular compounds in combinations with polymers allows one to manipulate practically all main properties of the OLEDs such as the emission color, type of charge carriers, control over the excitation energy transfer, and others, including the above-mentioned useful polymer properties. In addition, the low-molecular compounds which have 2–3 chromophore groups and are disposed to make glassy optically homogenous films are sufficiently good for applications in photonics, particularly in organic light emitting diodes (OLEDs) [1,2]. On the other hand, as was mentioned, the ability to manipulate a type of the chromophore and its positional relationship allows one to get the allocation of energy states and the conversion possibility distribution optimal for an optoelectronic device. For example, we have already showed that the close location of the chromophore groups can lead, in some cases, to perturbations which induce the elevated possibility of the singlet-triplet conversion [3].

The derivatives of aza-compounds such as carbazole, phenothiazine, and indole are widely studied as potential components of organic electronic and optoelectronic devices [4–7]. The present paper deals with spectral investigations of specific carbazole-, phenotiazine-, and indole-containing low-molecular glass-forming compounds, i.e., 3-(9-carbazolyl)-9-ethylcarbazole (JS-50), 3-(9-pheothiazinyl)-9-ethylphenothiazine (JS-57), 3-(9-pheothiazinyl)-9-ethylcarbazole (JS-51), and 3-(9-carbazolyl)-9-ethylphenothiazine (JS-54).

2. Objects and Experiment

The synthesis and the characterization of 3-(9-carbazolyl)-9-ethylcarbazole (JS-50), 3-(9-pheothiazinyl)-9-ethylphenothiazine (JS-57), 3-(9-pheothiazinyl)-9-ethylcarbazole (JS-51), and 3-(9-carbazolyl)-9-ethylphenothiazine (JS-54) are described in the previous publication [8].

The luminescence, phosphorescence, and absorption spectra of solutions and solids (powder and films) were investigated at room temperature and 77 K. Tetrahydrofuran (THF) was used as a solvent. UV-visible spectroscopy was used to determine the position of the first singlet and triplet energy states. Spectra of the studied compounds were acquired from a spectrophotometer Specord UV VIS. The solution concentrations for luminescence and phosphorescence measurements were $2.8 \cdot 10^{-3}$ M for JS-50 and JS-51, $2.4 \cdot 10^{-3}$ M for JS-57, and $2.6 \cdot 10^{-3}$ M for JS-54. Luminescence and phosphorescence measurements were carried out on a laboratory-made experimental setup with standard 90° geometry. The excitation source for luminescence and phosphorescence measurements was a nitrogen laser ($\lambda_{em.} = 337$ nm).

3. Results and Discussion

3.1. *3-(9-carbazolyl)-9-ethylcarbazole (JS-50)*

The molecule of JS-50 (Fig. 1) consists of one ethyl and 2 carbazolyl groups whose π-electron systems influence each other and determine its spectral properties.

The absorption spectrum of the compound solution is very similar to that of ethylcarbazole by the spectral position and shape [9,10]. The last one (ethylcarbazole) is a low-molecular analog of a JS-50 molecule. (Fig. 2). Luminescence band, contrary to the absorption peaks, has practically no vibration structure for both room temperature and 77 K, which means that carbazole groups in JS-50 is close enough to influence the electronic state of each other in excited states. This influence leads to a vibration structure destructurization of the basic electronic energy state when the molecule is excited.

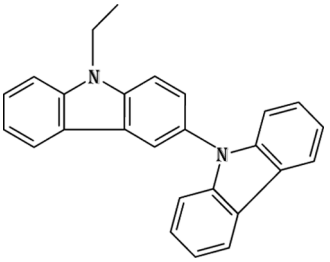

Figure 1. Molecule of JS-50.

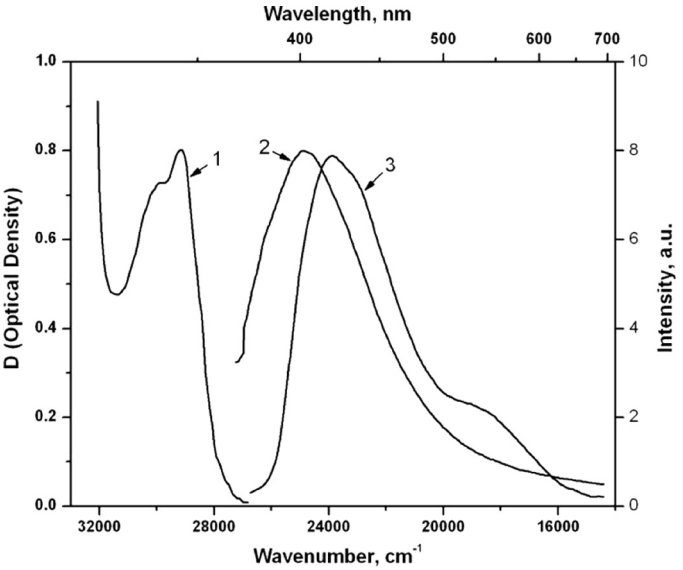

Figure 2. 1-solution optical absorption ($C = 9.2 \cdot 10^{-5}$ M) and 2,3-luminescence (solution, solid) of JS-50 in THF at 293 K ($\lambda_{ex.} = 337$ nm).

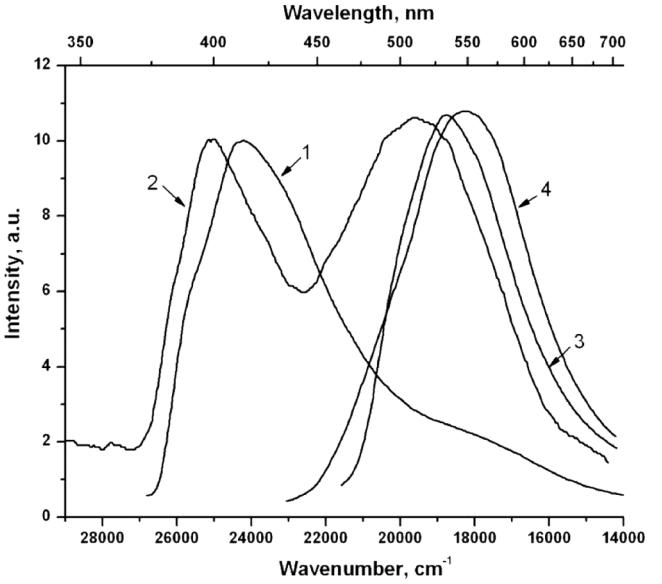

Figure 3. 1,2-luminescence (solution, solid) and 3,4-phosphorescence (solution, solid) spectra of JS-50 at 77 K ($\lambda_{ex.} = 337$ nm).

The absorption and luminescence spectra of a JS-50 molecule allow us to suppose that carbazolyl groups emit photons like the one π-electron system.

From spectral data, we estimate the position of the first singlet and triplet energy levels:

$E_{S1} \approx 3.4$ eV (or $\lambda = 361$ nm; $\tilde{\nu} \approx 27700\,cm^{-1}$), $E_{T1} \approx 2.7$ eV (or $\lambda = 458$ nm; $\tilde{\nu} \approx 21800\,cm^{-1}$) (Fig. 4).

It should be mentioned that, for the luminescence spectra of solids at 77° K, the intensities of fluorescence and phosphorescence peaks are almost equal (Fig. 3). This indicates a relatively high probability of the singlet-triplet (intercombinatory) conversion in JS-50 at a low temperature (77° K) in the solid state.

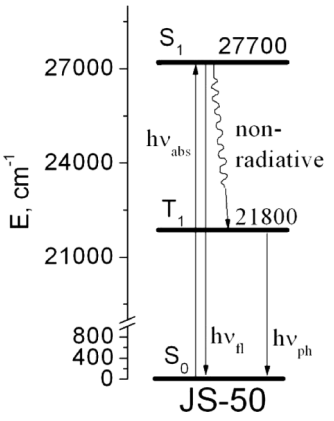

Figure 4. JS-50 energy levels.

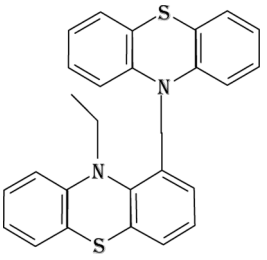

Figure 5. JS-57 molecule.

3.2. *3-(9-pheothiazinyl)-9-ethylphenothiazine (JS-57)*

The molecule of JS-57 (Fig. 5) is a dimer of phenotiazinyl groups.

The absorption spectum of a JS-57 solution is very similar to that of alkylphenotiazine [11]. That allows us to conclude that phenotiazine groups absorb light mainly like independent centers.

These spectra show a great contribution of phosphorescence to the total luminescence spectrum at 77° K. Like that for the previous molecules, this indicates the high effeciency of the intercombinatory conversion in the triplet state for a JS-57 solution at 77° K.

The luminescence of JS-57 in the solid form has characterically a sufficiently higher (as compared with fluorescence) phosphorescence contribution to the luminescence spectra at 77° K (Fig. 7).

We notice that the luminescence spectra of JS-57 solutions at both temperatures (293 and 77°K) are almost similar (by shape and spectral position) to the luminescence spectra of solids. This fact coupled with the absorption spectrum allows

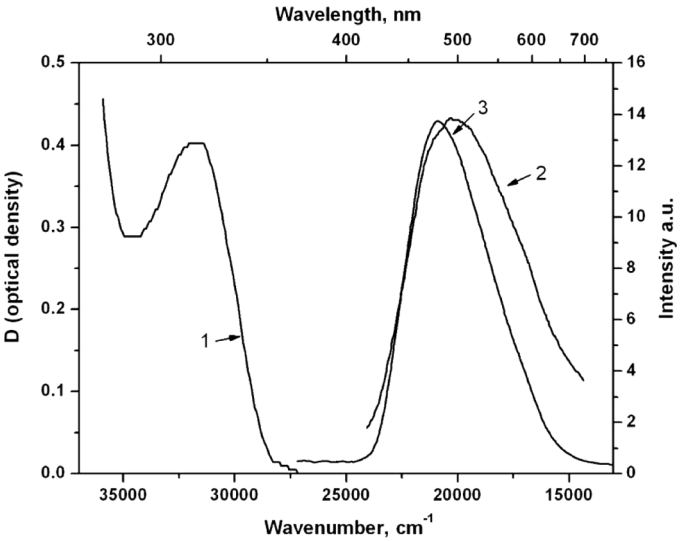

Figure 6. 1-solution optical absorption ($C = 1.5 \cdot 10^{-4}$ M) and 2,3-luminescence (solution, solid) of JS-57 in THF at 293 K ($\lambda_{ex.} = 337$ nm).

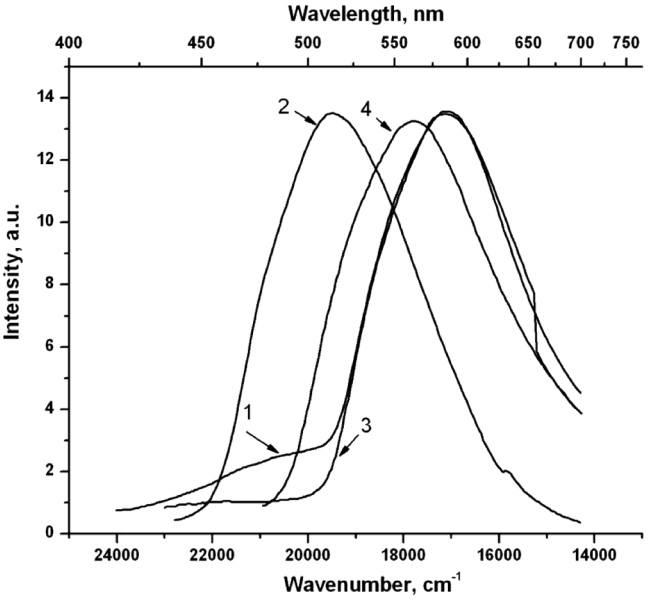

Figure 7. 1,2-luminescence (solution, solid) and 3,4-phosphorescence (solution, solid) spectra of JS-57 at 77 K ($\lambda_{ex.} = 337$ nm).

us to consider that phenotiazine groups in a JS-57 molecule do not interact between each other and behave like separate spectral centers.

The position of the first singlet and triplet energy levels for JS-57 are as follows: $E_{S1} \approx 3.4$ eV (or $\lambda = 366$ nm; $\tilde{\nu} \approx 27300\,cm^{-1}$), $E_{T1} \approx 2.5$ eV (or $\lambda = 495$ nm; $\tilde{\nu} \approx 20200\,cm^{-1}$), respectively (Fig. 8).

3.3. *3-(9-pheothiazinyl)-9-ethylcarbazole (JS-51)*

A JS-51 molecule (Fig. 9) consists of ethyl, carbazolyl, and phenothiazinyl groups which arrange the π-electron system of the molecule. Unlike the previous molecules,

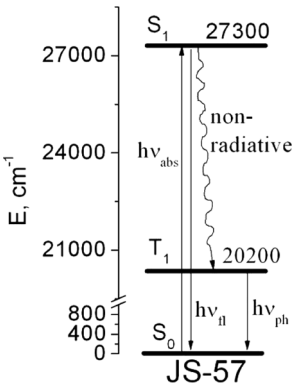

Figure 8. JS-57 energy levels.

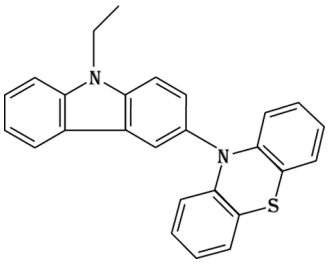

Figure 9. JS-51 molecule.

the absorption spectrum of a JS-51 solution has one broad peak without vibration structure at $\approx 29000\,cm^{-1}$ (Fig. 10). The position of this absorption peak is close to the ethylcarbazole long-wavelength absorption peak ($\approx 29000\,cm^{-1}$), but its shape looks more like the phenotiazine absorption peak at $\nu \approx 31000\,cm^{-1}$.

So, the two possible interpretations are proposed: 1) π-electron systems of carbazole and phenothiazine groups interact, by perturbing each other; 2) absorption spectrum of a JS-51 molecule is a result of the overlapping of the absorption by independent carbazole and phenotiazine groups. A more precise analysis should be made to make a substantiate decision between these two interpretations.

The luminescence of JS-51 in a solution is characterized by the long-wavelength peak domination both at room temperature and at 77° K (Figs. 10 and 11). The analogous behavior is observed for the low-temperature luminescence of solid JS-51 (Fig. 11).

We should say that the luminescence of a JS-51 solution does not show any vibration structure like it for a JS-50 molecule and contrary to the ethyl-carbazole analog.

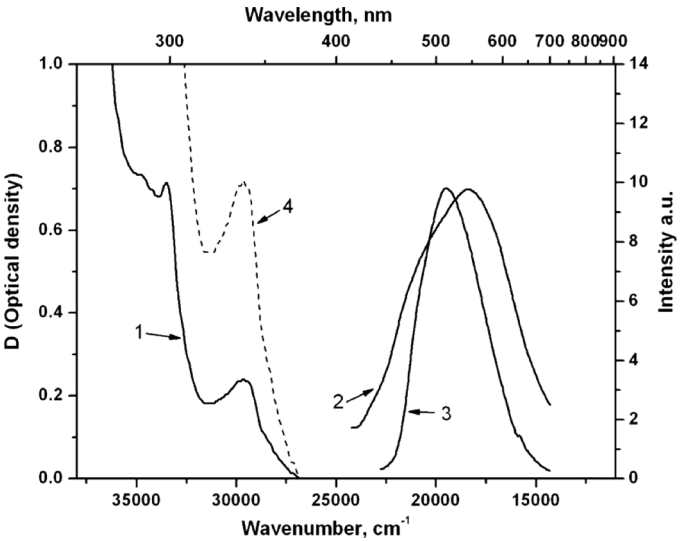

Figure 10. 1,4(x 3)-solution optical absorption ($C = 3.6 \cdot 10^{-6}\,M$) and 2,3-luminescence (solution, solid) of JS-51 in THF at 293 K ($\lambda_{ex.} = 337\,nm$).

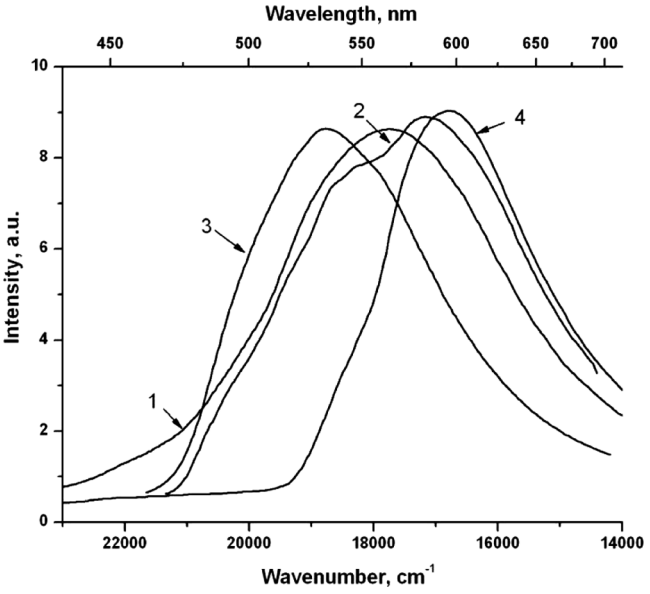

Figure 11. 1,2-luminescence (solution, solid) and 3,4-phosphorescence (solution, solid) spectra of JS-51 at 77 K ($\lambda_{ex.} = 337$ nm).

The position of the first singlet and triplet energy levels are: $E_{S1} \approx 3.3$ eV (or $\lambda = 372$ nm; $\tilde{\nu} \approx 26900\,cm^{-1}$), $E_{T1} \approx 2.7$ eV (or $\lambda = 463$ nm; $\tilde{\nu} \approx 21600\,cm^{-1}$), respectively (Fig. 12).

3.4. *3-(9-carbazolyl)-9-ethylphenothiazine (JS-54)*

Like the previous case, a molecule JS-54 consists of 3 groups (Fig. 13): ethyl, carbazolyl, and phenothiazinyl, but the last two functional groups are placed in the opposite position relative to the ethyl group.

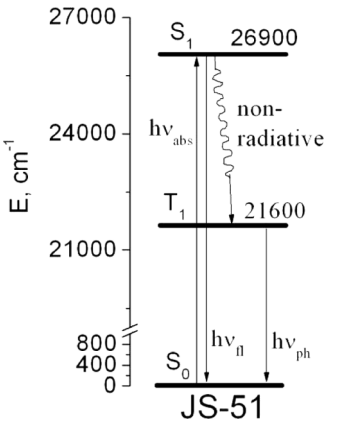

Figure 12. JS-51 energy levels.

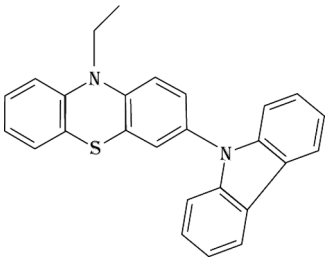

Figure 13. JS-54 molecule.

The low-temperature luminescence of the solution of JS-54 is similar to that of JS-51. Like that for JS-51, the phosphorescence of a JS-54 solution essentially dominates in the luminescence spectrum at 77° K (Fig. 15). However, for the solution phosphorescence at room temperature, the contribution to the luminescence spectrum is negligible (Fig. 14).

For the low-temperature luminescence of the solid sample, the position of the delayed emission peak is in the fluorescence spectral range, but with the emission delay time much longer than it usually takes for the fluorescence (Fig. 15). In our opinion, this caused by the triplet energy transfer and the following delayed fluorescence.

The questions, why the delayed fluorescence appears in solid JS-54 and which nature the traps of triplet excitons have remained unclear for now.

The positions of the first singlet and triplet energy levels were obtained from spectral data. They are: $E_{S1} \approx 3.4\,eV$ (or $\lambda = 369\,nm$; $\tilde{\nu} \approx 27100\,cm^{-1}$), $E_{T1} \approx 2.5$ eV (or $\lambda = 500\,nm$; $\tilde{\nu} \approx 20000\,cm^{-1}$), respectively (Fig. 16).

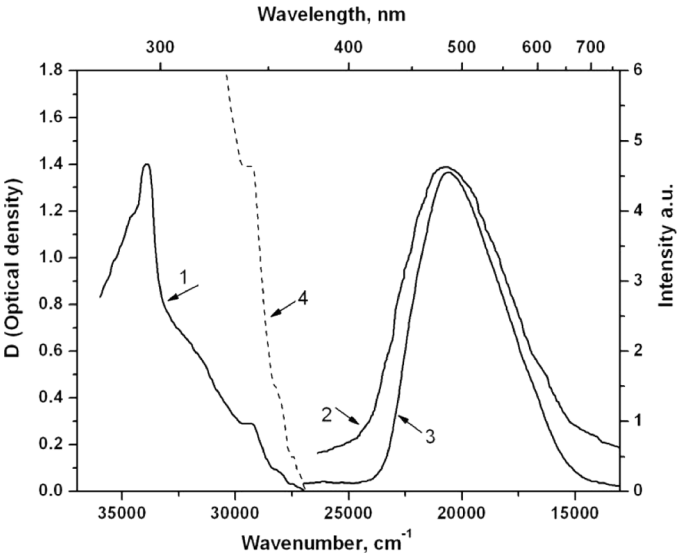

Figure 14. 1,4(x4,8)-solution optical absorption ($C = 2.1 \cdot 10^{-4}$ M) and 2,3-luminescence (solution, solid) of JS-54 in THF at 293 K ($\lambda_{ex.} = 337\,nm$).

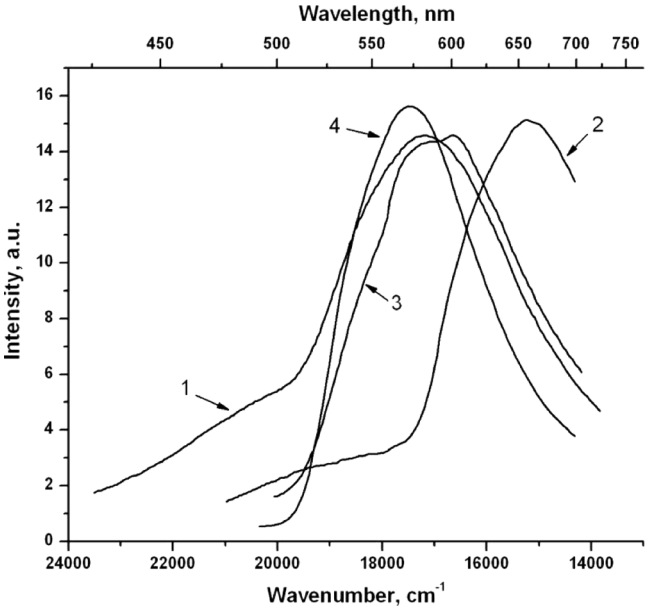

Figure 15. 1,2-luminescence (solution, solid) and 3,4-phosphorescence (solution, solid) spectra of JS-54 at 77 K ($\lambda_{ex.} = 337$ nm).

Analyzing the spectral behaviors of similar molecules JS-51 and JS-54, we find them quite different. Taking the differences in the molecular structures of these molecules into account, namely the opposite position of carbazole and phenothiazine groups relative to ethyl group, allows us to conclude that a position of the ethyl group and the positional relationship of π-electron-containing groups are crucial for spectral properties of these molecules. We consider that the carbazole and phenotiazine groups in JS-51 and JS-54 do not act like separate spectral centers and influence each other.

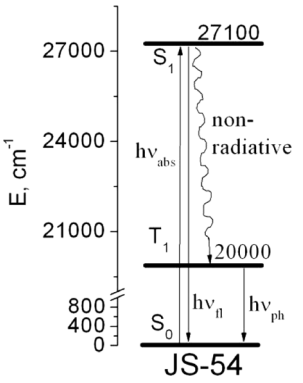

Figure 16. JS-54 energy levels.

4. Conclusions

1. The location of the first singlet and triplet energy levels of specific carbazole- and phenothiazine-containing glass-forming compounds, i.e., 3-(9-carbazolyl)-9-ethylcarbazole (JS-50), 3-(9-pheothiazinyl)-9-ethylphenothiazine (JS-57), 3-(9-pheothiazinyl)-9-ethylcarbazole (JS-51), and 3-(9-carbazolyl)-9-ethylphenothiazine (JS-54) have been obtained from the spectral data; the schemes of electronic processes in the corresponded bulk materials caused by chromophore excitations have been proposed. A high probability of the intercombinatory transition to the triplet state for compounds JS-51, JS-54, and JS-57 at $T = 77^{\circ}$ K, as well in solid state and in solution, has been observed. The dominating spectral band which corresponds to the T_1 (S_0 transition in luminescence spectra of the above-mentioned compounds at $T = 77^{\circ}$ K is the evidence of these facts.
2. The centers of absorption and fluorescence for 3-(9-carbazolyl)-9-ethylcarbazole (JS-50), 3-(9-pheothiazinyl)-9-ethylphenothiazine (JS-57) have been identified. The similarity of the luminescence spectra of the solutions of JS-57 to the luminescence spectra of its solid samples at different temperatures has been stated. This observation indicates a weak interaction both in solutions and in the solid state and shows the electron excitation transfer processes are not significant. The spectral location of the delayed emission spectra of compound 3-(9-carbazolyl)-9-ethylphenothiazine (JS-54) corresponds to the fluorescence band that can be interpreted as the delayed fluorescence.
3. The relative arrangement of energy triplet levels of the studied compounds points to a more perspective using of 3-(9-carbazolyl)-9-ethylcarbazole (JS-50) and 3-(9-pheothiazinyl)-9-ethylcarbazole (JS-51) for transport layers, particularly in OLEDs.

Acknowledgment

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