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DEVELOPMENT OF WHITE ORGANIC LIGHT EMITTING DIODES BASED ON CARBAZOLE-DERIVED COMPOUNDS

The object of research is the thermal, photophysical, and electrophysical properties of newly synthesized carbazole-derived compounds and organic light-emitting structures based on them. The problem consists in the comprehensive solution of scientific and technical problems of improving the characteristics of white organic light-emitting diodes (OLED), expanding their emission spectrum, improving color and energy characteristics.

The results of the thermal, electrophysical and photophysical properties of the investigated carbazole compounds were obtained. They demonstrated good thermal stability. Absorption spectra in solid films were recorded in the range of 300–350 nm. Photoluminescence spectra were observed at a wavelength of 407 nm for the first and second compounds and 430 nm for the third. The quantum yield of photoluminescence in films for compounds 1, 2, and 3 was 16 %, 7 %, and 7 %, respectively.

Organic light-emitting structures of white emission color with color coordinates (0.31, 0.35), (0.32, 0.34) and (0.38, 0.34) close to natural white light (0.33, 0.33) were formed using the thermovacuum sputtering method. The turn-on voltage of the white OLED is 6 V, the maximum brightness of the light-emitting structures was 10,000 cd/m^2. The devices demonstrated a sufficiently high external quantum efficiency of 5 % to 7 %.

The obtained results are explained by the mixing of different types of electroluminescence, namely excitonic and electromeric. Electromeric radiation is obtained due to transport layers. This approach improves such an important parameter of white light as its quality, which includes color coordinates and color rendering index.

Due to their color characteristics, white light-emitting diodes based on carbazole-derived compounds are promising candidates for use in modern lighting systems. A separate advantage of these light-emitting structures is the dependence of the color gamut of their radiation on the applied voltage. In addition, organic LEDs based on carbazole-derived compounds have low energy consumption and are environmentally friendly due to the absence of toxic substances in their design, which creates prerequisites for both global energy savings and a reduction of the industrial burden on the environment.

Keywords: *organic light emitting diodes, OLED, electroplex, carbazole-derived compounds, thermogravimetry, differential scanning calorimetry, electroluminescence.*

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1. Introduction

The development of organic light-emitting diodes (OLED) technologies is due to the commercial attractiveness of displays and lighting systems based on them. They have a number of advantages, as low energy consumption, the absence of toxic substances in their design, which creates prerequisites for global energy savings, as well as low cost of production.

The choice of donor and acceptor components for OLED's structures plays an important role in the optimal operation of the devices. Today there are examples of successful use of carbazole, phenoxazine, phenazine and acridine as emitters for OLEDs [1, 2].

There are already examples of white organic LEDs based on such systems that demonstrate high power and quantum efficiency [1–6]. Color-tunable white OLEDs have potential applications for lighting systems. They make it possible to widely adjust emission coordinates, color temperatures, and color rendering indices by applying different voltages [3–5]. There are a number of requirements for fluorescence materials used in the development of OLED devices, such as high and balanced charge mobility, thermal stability, HOMO and LUMO energy levels.

The aim of the research is to develop methods for simplifying the structures of white organic LEDs with the possibility of adjusting their color coordinates. This will make it possible to create new white organic light-emitting structures with fewer functional layers and improved color characteristics.

This work presents the results of using a series of carbazole-derived compounds as emitter layers in white organic LEDs.

2. Materials and Methods

An analysis of the main characteristics of newly synthesized carbazole-derived compounds as potential candidates for use in OLEDs was carried out. To determine the energy levels of the studied compounds, the method of cyclic voltammetry (CV) was used by applying positive and negative voltage using a Bio-Logic three-electrode cell and a Bio-Logic SP potentiostat-galvanostat.

The study of the thermal properties of the compounds was carried out by the method of differential scanning calorimetry (DSC) on a commercial Perkin-Elmer DSC differential scanning calorimeter. The heating rate of the samples was maintained at 10 °C/min for melting and decomposition of molecules in a nitrogen atmosphere at a flow rate of 30 ml/min.

Optical absorption spectra were studied using a Shimadzu UV-2450 spectrophotometer. The source of radiation of the spectrophotometer is an arc xenon lamp, the radiation of which passes through a double monochromator and a photomultiplier, falls on the cuvette with the sample under investigation and, after that, is fixed by the detection device.

The thermovacuum deposition method was used to produce OLED structures to obtain thin, uniform organic films on an ITO substrate. Sputtering of functional films was carried out layer by layer using a UVR-3M vacuum sputtering unit. Control of the film thickness was carried out by the quartz resonator method.

3. Results and Discussions

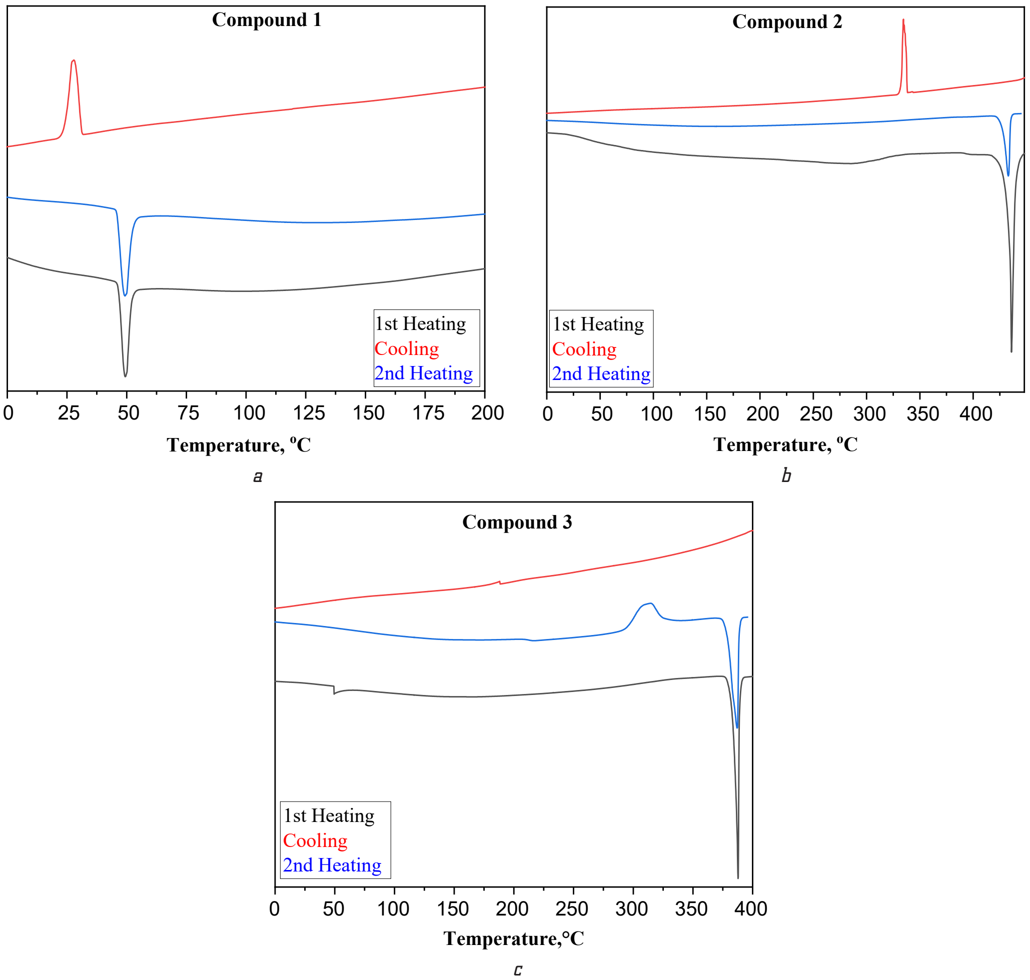
3.1. Thermal properties. The first step of the research of carbazole-derived compounds is the study of their thermal characteristics for further coordination of the temperature regimes of film formation. For this, the methods of thermogravimetric analysis and differential scanning calorimetry were applied. Compound 1, compound 2 and compound 3 showed good thermal stability as the five percent mass loss temperatures were 362 °C, 411 °C and 409 °C, respectively.

All samples were obtained as crystalline samples. However, sample 1 showed a significantly lower melting point of 49 °C. Sample 2 and sample 3 exhibited melting points of 432 °C and 386 °C, respectively (Fig. 1, *b*, *c*).

At 28 °C, sample 1 started to form crystals, while sample 2 started to form crystals at 334 °C and sample 3 at 311 °C. In addition, a melting point of 432 °C was recorded for sample 2, which exceeds the temperature of five percent mass loss, indicating a sublimation process of the compound. Glass transition temperatures were not recorded for samples 1 and 2, which means that they do not have the properties of molecular glass formation.

3.2. Photophysical properties. The photophysical properties of carbazole-derived compounds 1–3 were studied using stationary absorption and photoluminescence spectroscopy (Fig. 2). Absorption and photoluminescence spectra were recorded from solid films.

Absorption spectra (Fig. 2, *a*) showed similar shapes for all three compounds in the range of 300–350 nm. The low-energy band shows clear vibrational structures with well-separated 0–0 and 0–1 transitions at 335 and 322 nm, respectively.

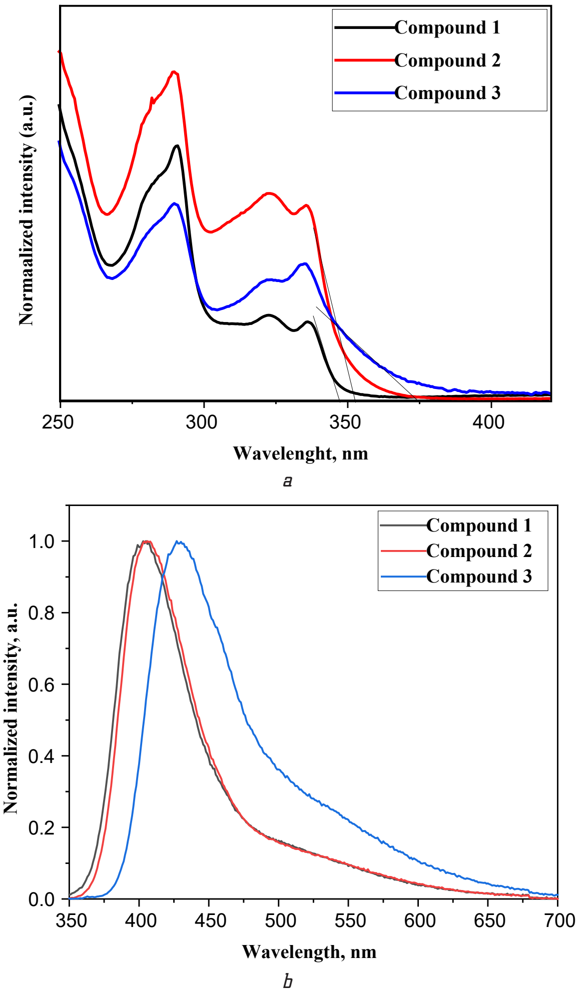


a

b

c

Fig. 1. Results of thermogravimetric analysis of carbazole-derived compound: *a* – 1; *b* – 2; *c* – 3



a

b

Fig. 2. Spectra of solid films of carbazole-derived compounds: *a* – absorption; *b* – photoluminescence

The 0–2 transition at 309 nm is also visible in a separate «shoulder». These transitions originate from locally excited states of carbazole [6, 7]. Since the locally excited states of the pyridine moieties are at wavelengths below 300 nm, overlapping pyridine causes absorption at energies higher than 4.1 eV.

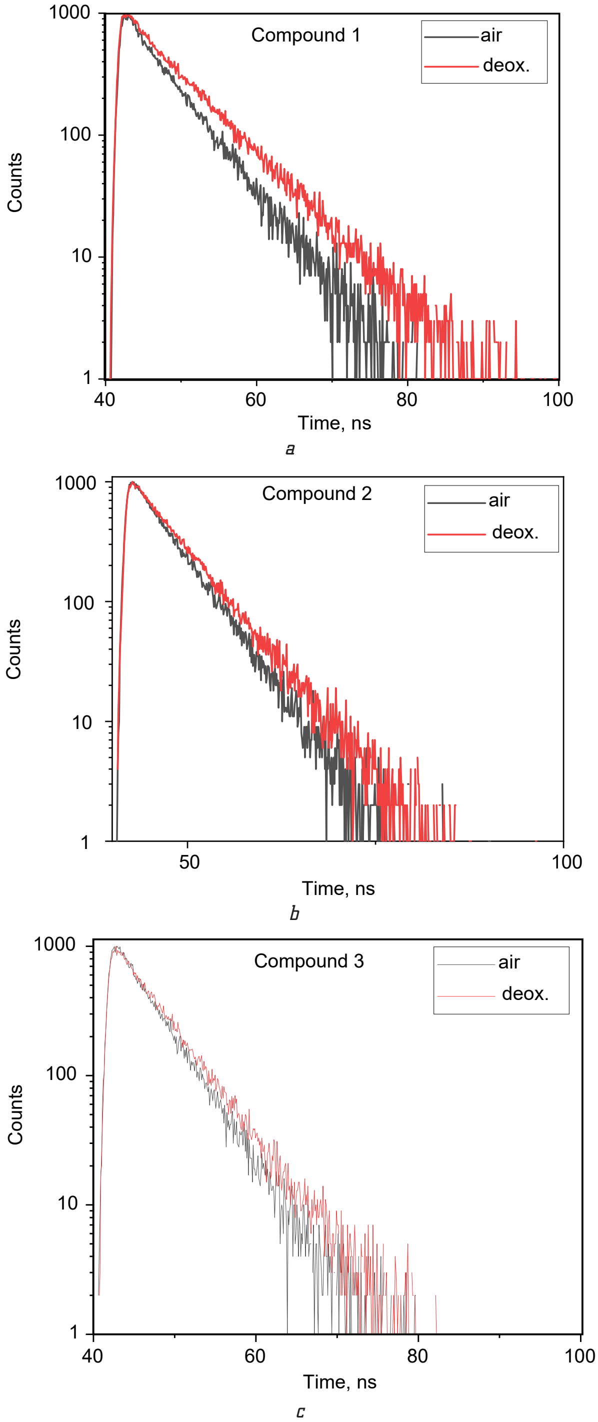
The photoluminescence spectra in the films (Fig. 2, *b*) demonstrated a tendency to the red-shifted in visible region. The photoluminescence wavelength maxima for compound 1 and compound 2 were observed at 407 nm, while the photoluminescence of compound 3 was red-shifted and recorded at 430 nm. The recorded values of the photoluminescence quantum yield in the films for 1, 2, and 3 compounds were 16 %, 7 %, and 7 %, respectively (Table 1).

Table 1

Photophysical properties of carbazole-derived compounds

		Compound 1	Compound 2	Compound 3
Wavelength of *PL* max, nm	Film	407	407	430
Φ_{PL}, %		16	7	7

Photoluminescence times decay demonstrated the sensitivity of compounds to oxygen, which may be related to the ability of compounds to assemble triplets through the hybridization of locally excited states and charge transfer states [8]. This assumption is consistent with the emission behavior of compounds in films (Fig. 2, *b*). Fig. 3 shows the photoluminescence decay times. It can be seen that the photoluminescence lifetime increases as the emission wavelengths increase from the band of maximum to the «shoulder».



a

b

c

Fig. 3. Photoluminescence times decay of carbazole-derived compounds: *a* – 1; *b* – 2; *c* – 3

In addition, the photoluminescence lifetime is also dependent on air and increases after deoxygenation of the samples.

3.3. Characteristics of OLED devices. The idea of expanding the OLED emission spectrum based on carbazole-derived compounds with a minimum number of functional layers is based on the ability of some transport layers to generate electroluminescent radiation of electroplex origin in the long-wave spectrum region [9]. This approach partially improves such an important parameter of white light as its quality, which includes CIE coordinates and color rendering index (CRI). The formation of the structure of the devices took placing layer by layer and co-deposition (Compound 1–3:DPEPO) by the thermovacuum deposition method. The energy diagram of the devices is shown in Fig. 4.

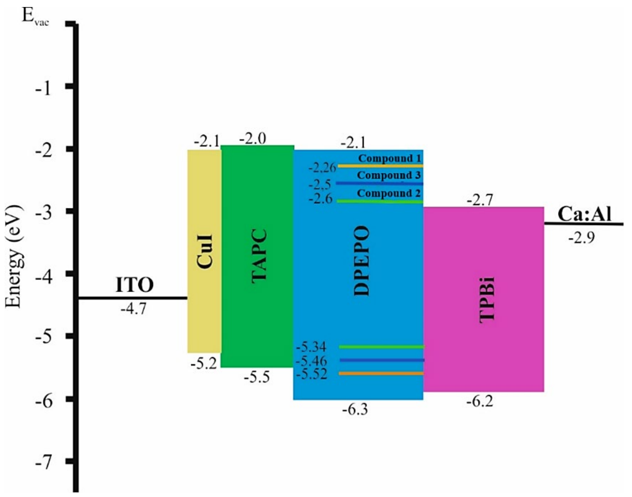


Fig. 4. Energy diagram of the developed OLEDs

The materials used for the production of white OLEDs were: CuI as a hole injection layer [10], 4,4′-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC) as hole transport layer [11]. Bis[2-(diphenylphosphino) phenyl] ether oxide (DPEPO)), an organic semiconductor widely used as a host material for TADF-based blue organic LEDs, served as a matrix for the emitting carbazole-derived compounds 1, 2, and 3 [12]. The 1,3,5-tris (n-phenyl benzimidizol-2-yl) benzene (TPBI) film is used as an electron transport layer, which ensures the drift of electrons from the Ca:Al cathode to the light-emitting layer.

The electroluminescence spectra of the devices shown in Fig. 5 are characterized by wide emission maxima of various nature. White electroluminescence is achieved due to overlapping of the emissions of compounds and to the different intensities of electroplex emission of the hole-transporting layer under different applied voltages.

The first band of short-wave radiation with a maximum at 407 nm, 410 nm and 430 nm is characteristic of the main exciton emission of emitters 1–3, respectively, for devices 1–3. The long-wavelength band of electroluminescence with a maximum of 580 nm should be attributed to the radiation in TAPC, in which the spatial cross-radiative recombination of electromers leads to a strong red-shifted of the emission spectrum in comparison with the spectra emitted by molecular excitons and electromers [9, 13, 14].

The stability of the electroluminescence spectra of devices 1–3 tested at different voltages is rather mediocre, which may indicate the presence of conformational disorder effects that could occur at different control voltages (Fig. 5). Analyzing the balance energy diagram of WOLED structures 1–3 (Fig. 4), it can be noted that the zone of radiative recombination of both excitons is located in the light-emitting layers (DPEPO: Compound 1 (Device 1), DPEPO: Compound 2 (Device 2) or DPEPO: Compound 3 (Device 3)).

The TAPC film additionally performs the role of a second light-emitting layer – an electroplex emitter, which is activated by a low energy barrier for the drift of electrons from the cathode. Main emission with electroplex emission of the hole-transporting layer, is demonstrated to be useful for the development of white OLED with external quantum efficiency of up to 5.2 %.

The current density and brightness versus voltage curves are shown in Fig. 6. The high turn-on voltages were observed for doped devices 1–3 (Fig. 6, *a*), possibly indicating a wide area of device electroluminescence emission for all manufactured WOLEDs. The main parameters of the developed OLED devices are listed in Table 2.

In addition to high-quality white electroluminescence, high EQE values were observed as for white OLEDs. The highest values of maximum power, current and quantum efficiency were observed for device 3 (Fig. 3, *a*, *b*, Table 2). It also showed a high brightness of ~9000 cd/m^2 at 14.5 V.

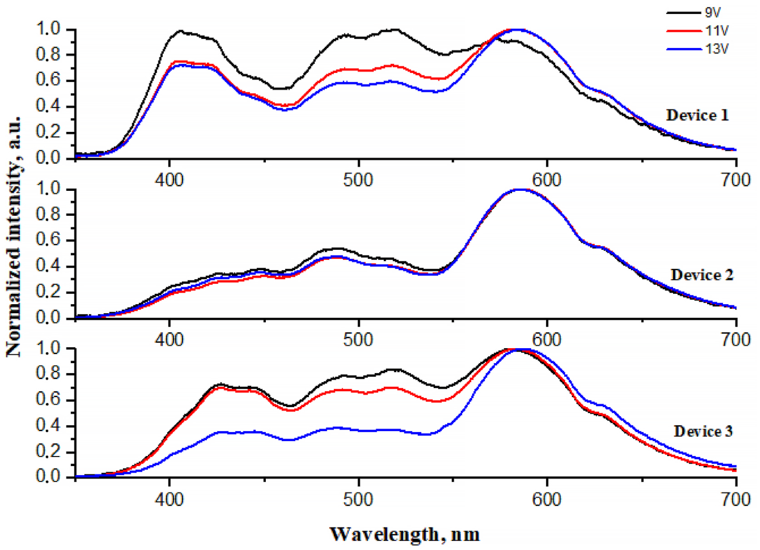
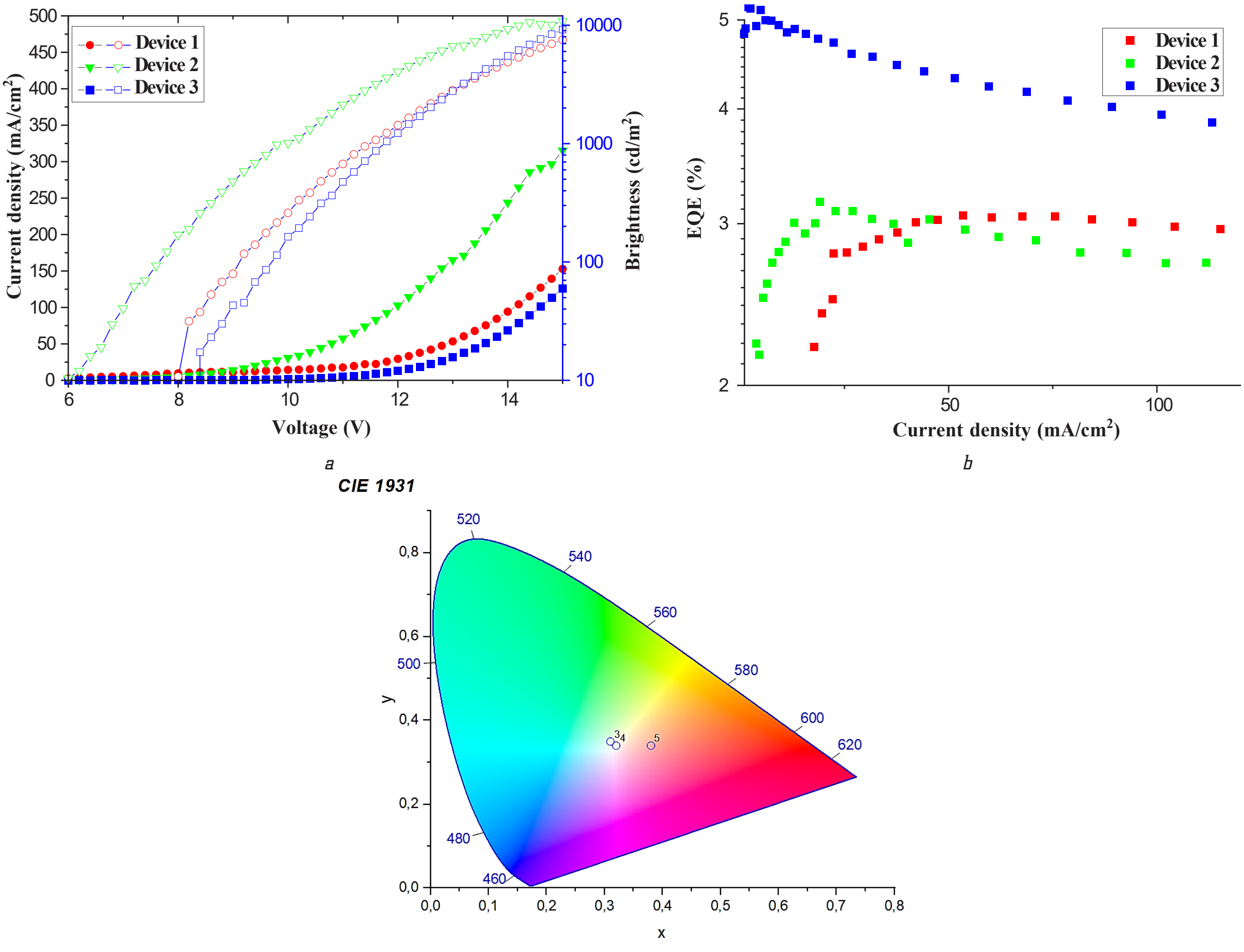


Fig. 5. Electroluminescence spectra of white OLEDs based on carbazole-derived compounds



a

b

c

Fig. 6. Manufactured OLEDs 1–3: *a* – curves of dependence current density and brightness on voltage; *b* – dependence external quantum efficiency on current density; *c* – CIE 1931 color diagram

Table 2

Parameters of OLED devices based on carbazole-derived compounds

Devices	V_{ON} (V)	EQE_{max} (%)	CE_{max} (cdA^{-1})	Brightness (cd/m^2)	CIE
1	6	3.06	5.27	7526.44	(0.31, 0.35)
2	7	3.09	5.45	10804.53	(0.32, 0.34)
3	10	5.3	10.6	9181.26	(0.38, 0.34)

3.4. Discussion. In recent years, there has been a tendency to replace existing light sources with lighting systems based on OLED white light emission with characteristics (color quality, Commission International d'Eclairage coordinates, color temperature and color rendering index) close to natural white light. Although the WOLED fabrication technology has reached the commercialization stage, the methods to optimize the emission color quality continue to be improved and new device architecture approaches are created to improve energy efficiency and color quality. In this context, the use of WOLED technology with a simplified structure is extremely promising. For this purpose, compounds 1, 2, and 3 were tested as a light-emitting layer of an organic LED. Electroluminescence studies of bilayer devices based on compounds 1, 2, and 3 demonstrate a good possibility of color tuning due to the formation of an electroplex with DPEPO. In the devices, it was found that the coherent volume and electroplex emissions are very sensitive to the applied voltage. At the same time, the devices demonstrate effective light-emitting characteristics and high color stability, which will be very useful for use in the modern lighting systems and display technologies.

The main limitation of applicability of the obtained results is the high cost of introducing lighting systems based on the studied compounds into mass production. Moreover, the gradual degradation of the light-emitting layer during operation causes a decrease in efficiency and a change in spectral characteristics.

It should be noted that for the further implementation of the obtained WOLEDs as basic elements in the modern lighting systems, it is necessary to carry out complex works, in particular, to refine the technology of thermovacuum application of functional light-emitting structures on industrial installations and to obtain large areas of OLED matrices, etc.

While performing the research presented in the work, we encountered the problem of power outages caused by the war in Ukraine, which affected the technological process of manufacturing light-emitting devices and, possibly, had consequences in the deterioration of the output parameters of organic LEDs.

4. Conclusions

The results of studies of thermal, photophysical and electroluminescent properties of three new carbazole derivatives are given. The compounds show photoluminescence quantum yield of the solid film 16 % as a result of relaxation of hybridized local states and charge transfer states. The white electroluminescence with an adjustable color is achieved due to the overlapping of the radiation of the investigated compounds and the electroplex radiation of the hole transport layer. White organic light-emitting diodes with adjustable color have been developed. The devices demonstrated an external quantum efficiency of 3.06 %, 3.09 %, 5.3 % with color coordinates (0.31, 0.35), (0.32, 0.34), and (0.38, 0.34) respectively, close to natural white light (0.33, 0.33), obtained by mixing exciton and electroplex type of emission.

Conflict of interest

The authors declare that they have no conflict of interest concerning this research, whether financial, personal, authorship or otherwise, that could affect the study and its results presented in this paper.

Financing

The study was performed without financial support.

Data availability

The paper has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating this work.

References

1. Zhang, Q., Li, B., Huang, S., Nomura, H., Tanaka, H., Adachi, C. (2014). Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence. *Nature Photonics, 8 (4),* 326–332. doi: https://doi.org/10.1038/nphoton.2014.12
2. Ledwon, P. (2019). Recent advances of donor-acceptor type carbazole-based molecules for light emitting applications. *Organic Electronics, 75,* 105422. doi: https://doi.org/10.1016/j.orgel.2019.105422
3. Zhang, X., Pan, T., Zhang, J., Zhang, L., Liu, S., Xie, W. (2019). Color-Tunable, Spectra-Stable Flexible White Top-Emitting Organic Light-Emitting Devices Based on Alternating Current Driven and Dual-Microcavity Technology. *ACS Photonics, 6 (9),* 2350–2357. doi: https://doi.org/10.1021/acsphotonics.9b00900
4. Joo, C. W., Moon, J., Han, J.-H., Huh, J. W., Lee, J., Cho, N. S. et al. (2014). Color temperature tunable white organic light-emitting diodes. *Organic Electronics, 15 (1),* 189–195. doi: https://doi.org/10.1016/j.orgel.2013.10.005
5. Yang, S.-H., Shih, P.-J., Wu, W.-J., Huang, Y.-H. (2013). Color-tunable and stable-efficiency white organic light-emitting diode fabricated with fluorescent-phosphorescent emission layers. *Journal of Luminescence, 142,* 86–91. doi: https://doi.org/10.1016/j.jlumin.2013.03.060
6. Wong, K.-T., Chen, Y.-M., Lin, Y.-T., Su, H.-C., Wu, C. (2005). Nonconjugated Hybrid of Carbazole and Fluorene: A Novel Host Material for Highly Efficient Green and Red Phosphorescent OLEDs. *Organic Letters, 7 (24),* 5361–5364. doi: https://doi.org/10.1021/ol051977h
7. Danyliv, Y., Ivaniuk, K., Danyliv, I., Bezvikonnyi, O., Volyniuk, D., Galyna, S. et al. (2023). Carbazole-σ-sulfobenzimide derivative exhibiting mechanochromic thermally activated delayed fluorescence as emitter for flexible OLEDs: Theoretical and experimental insights. *Dyes and Pigments, 208,* 110841. doi: https://doi.org/10.1016/j.dyepig.2022.110841
8. Li, W., Liu, D., Shen, F., Ma, D., Wang, Z., Feng, T. et al. (2012). A Twisting Donor-Acceptor Molecule with an Intercrossed Excited State for Highly Efficient, Deep-Blue Electroluminescence. *Advanced Functional Materials, 22 (13),* 2797–2803. doi: https://doi.org/10.1002/adfm.201200116
9. Kalinowski, J., Giro, G., Cocchi, M., Fattori, V., Di Marco, P. (2000). Unusual disparity in electroluminescence and photoluminescence spectra of vacuum-evaporated films of 1,1-bis ((di-4-tolylamino) phenyl) cyclohexane. *Applied Physics Letters, 76 (17),* 2352–2354. doi: https://doi.org/10.1063/1.126343
10. Shan, M., Jiang, H., Guan, Y., Sun, D., Wang, Y., Hua, J., Wang, J. (2017). Enhanced hole injection in organic light-emitting diodes utilizing a copper iodide-doped hole injection layer. *RSC Advances, 7 (22),* 13584–13589. doi: https://doi.org/10.1039/c6ra28644e
11. Miwa, T., Kubo, S., Shizu, K., Komino, T., Adachi, C., Kaji, H. (2017). Blue organic light-emitting diodes realizing external quantum efficiency over 25 % using thermally activated delayed fluorescence emitters. *Scientific Reports, 7 (1).* doi: https://doi.org/10.1038/s41598-017-00368-5
12. Xu, H., Wang, L.-H., Zhu, X.-H., Yin, K., Zhong, G.-Y., Hou, X.-Y., Huang, W. (2006). Application of Chelate Phosphine Oxide Ligand in EuIII Complex with Mezzo Triplet Energy Level, Highly Efficient Photoluminescent, and Electroluminescent Performances. *The Journal of Physical Chemistry B, 110 (7),* 3023–3029. doi: https://doi.org/10.1021/jp055355p
13. Stavrou, K., Danos, A., Hama, T., Hatakeyama, T., Monkman, A. (2021). Hot Vibrational States in a High-Performance Multiple Resonance Emitter and the Effect of Excimer Quenching on Organic Light-Emitting Diodes. *ACS Applied Materials & Interfaces, 13 (7),* 8643–8655. doi: https://doi.org/10.1021/acsami.0c20619
14. Wei, M., Gui, G., Chung, Y.-H., Xiao, L., Qu, B., Chen, Z. (2015). Micromechanism of electroplex formation. *Physica Status Solidi (b), 252 (8),* 1711–1716. doi: https://doi.org/10.1002/pssb.201552098

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