ІНФОКОМУНІКАЦІЙНІ ТЕХНОЛОГІЇ ТА ЕЛЕКТРОННА ІНЖЕНЕРІЯ
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ЕЛЕКТРОНІКА ТА ІНЖЕНЕРІЯ

THE DEVELOPMENT OF NON-DOPED OLED BASED ON DONOR-ACCEPTOR TETRACHLOROPYRIDINE-CARBAZOLE MATERIAL WITH THE EMISSION IN "DEEP-BLUE" REGION

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The development of efficient organic light emitting diodes (OLED) based on the phenomenon of intramolecular thermally activated delayed fluorescence (TADF), in the design of which there are no blue phosphorescent emitters based on rare earth metals, still remains a challenge in the development of new lighting systems and OLED displays. The article proposes a technological approach to the formation of new type of OLED, where the emitter is an organic donor-acceptor molecular material 9-(2,3,5,6-tetrachloropyridin-4-yl)-9H-carbazole (4-CzPyCl4), in which electronic interaction between the donor and acceptor fragment plays a key role in the mechanism of delayed fluorescence. The design of the developed light-emitting heterostructure uses layer-by-layer formation of functional nanosized organic films, in contrast to traditional OLED designs of dark blue color radiation, which uses a guest-host systemThe external quantum efficiency of the developed OLED is 2.8 %. The maximum brightness of 3,000 cd/m^2 is reached at a voltage of 15 V. The chromaticity coordinates CIE (x, y) 1931 are (0.15, 0.13), which corresponds to the "dark blue" emitting spectral zone.

Key words: *OLED; delayed fluorescence; exciton; electroluminescence; triplet states; external.*

1. Introduction

Low cost of production of light emitting diodes based on organic materials (compared to phosphorescent LEDs containing complexes based on rare earth metals), flexibility and simple design, wide radiation area with appropriate Joule heat distribution (operating current density is only tens of mA/cm^2 and it prevents heating of the structure and eliminates the need to install cooling radiator systems) created the preconditions for the widespread use of OLED as a basic element of the latest lighting systems [1, 2]. A big commercial potential also have full-color displays, the pixels of which are OLED structures of white glow. The electroluminescence of such light-emitting organic devices may include the total radiation of the three primary colors – red, green and blue (RGB). However, despite the significant progress made over the last decade in the field of organic electronics, the production of blue OLEDs remains an important issue [3, 4]. Today, there are at least three parameters that need to be optimized to improve the competitiveness of OLED, namely: efficiency, color quality and extended lifetime. You can improve the

parameters of OLED, taking into account the principle of its operation. Thus, electrons and holes injected from the cathode and anode of the light-emitting heterostructure, respectively, drift abruptly through organic disordered semiconductor layers. If charge carriers of different nature come close enough to each other, the Coulomb force causes them to capture each other, forming an exciton. The relaxing exciton forms an excited state belonging to either the singlet or triplet state. Since the injected electrons and holes have a random orientation of the spins, it is believed that the upper limit of the formation of singlet excitons does not exceed 25 % [5]. The key problem in this case is that in many materials for OLED singlet exciton will provide luminescence, while triplet – no. For this reason, there is an intensive search for the possibility of effective use of triplet excitons. It is known that radiative transition from triplet states is often prohibited, but this process can be quite effective in some materials, in particular organometallic, in which radiative transition from triplet state is possible in the case of non-radiative intercombined energy transfer S1 → T1 (intersystem crossing (ISC)). singlet in triplet states [6].

Unfortunately, the power supply applied to the OLED structure based on blue organometallic complexes to provide the level of brightness required for the operation of displays or lighting fixtures, negatively affects the lifetime of blue OLED [7]. This typical problem of high-performance blue phosphorescent OLEDs and the high cost of organometallic complexes forces the use of alternative methods to avoid spin inhibition, in particular thermally activated delayed fluorescence [8, 9]. The phenomenon of thermally activated delayed fluorescence (TADF) recently found great use due to the possibility of achieving high values of external quantum efficiency of OLED without the use of expensive rare earth organometallic complexes. Unlike ordinary, fast fluorescence, the peculiarity of slow fluorescence is that before the emission of a quantum of light, the molecule is in a triplet state for some time. Such TADF molecules are characterized by a small value of the energy gap (ΔEST) between the lower excited singlet and triplet states (S1 and T1) and a number of conditions are met to overcome the non-radiative quenching processes. The effect of TADF can be observed in donor-acceptor molecules (D-A) with a strong spatial gap between the donor acceptor fragments and the values of the luminescence rate constants exceeding 106 s^{-1}. In this case, from the long-lived state T1 to the radiating state S1, a channel of thermal activation of reverse intersystem crossing (RISC) is formed. Note that the intramolecular RISC (Fig. 1) is sensitive to the splitting ΔEST [9]. It is obvious that it is quite difficult to construct and synthesize a molecule that would meet the conditions of intramolecular RISC and could be used in OLED, especially those that emit blue light [10]. So, we offer design and technological approaches to the formation of OLED with radiation in “dark blue” spectral zone, which is based on intramolecular TADF, as well as the results of the study of the characteristics of the developed OLED. The emitter of the organic light-emitting heterostructure was the organic donor-acceptor molecular material 9-(2,3,5,6-tetrachloropyridin-4-yl)-9H-carbazole (4-CzPyCl4), the chemical structure of which is shown in Fig. 2 [11].

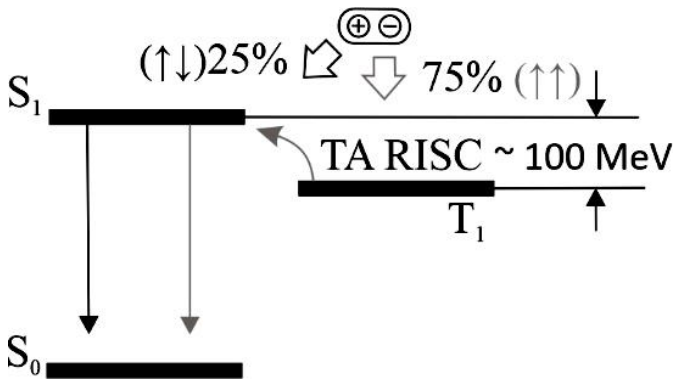

Fig. 1. Scheme of obtaining intramolecular TADF through TA RISC

The material was synthesized at Kaunas University of Technology (Lithuania) in the group of prof. Jozas Vidas Gražulevičius. The donor fragment of 4-CzPyCl4 is carbazole, and the acceptor component is tetrachloropyridine. The choice of 4-CzPyCl4 as a dark blue emitter was due to the presence of intramolecular TADF (ΔEST = 0.15 eV), a relatively high value of the quantum efficiency of photoluminescence (16 %), good heat resistance of the material, as well as an inexpensive one-step synthetic method.

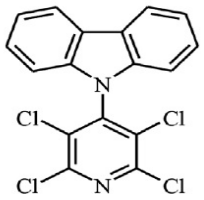

Fig. 2. Chemical structure of 4-CzPyCl4 [11]

2. Formation of light-emitting structure and experimental technique

To study the electroluminescent properties of 4-CzPyCl$_4$, a multilayer organic structure with functional layers, which are often used for the manufacture of OLED structures, was formed. The electroluminescent structure of ITO/CuI/ TCTA/4-CzPyCl4/TSPO1/TPBI/Ca/Al (Fig. 3) was formed in layers on the surface of a glass substrate with a layer of transparent semiconductor ITO (In_2O_3: SnO_2) in the chamber of vacuum thermal application with residue pressure of 1×10^{-3} Pa. The area of the obtained radiating structure was 3×6 mm^2. The dependences of current density on voltage and brightness were determined using a parametric analyzer HP 4145A. Brightness measurements were performed using a calibrated photodiode, which was calibrated according to the previously described method [12]. The photodiode was placed at a distance of 15 cm from the working OLED in a darkened room. Quantum efficiency values (EQE) were determined according to the method described in [13]. The electroluminescence spectrum of dark blue OLED was obtained using a USB2000 spectrometer.

After applying a direct electrical displacement to the structure of ITO/CuI/TCTA/4-CzPyCl4/TSPO1/TPBI/Ca/Al, holes are injected from the transparent anode (ITO layer) through the HOMO levels (highest occupied molecular orbital) of copper iodide layers (I) (CuI) and tris (4-carbazoyl-9-ylphenyl) amine (TCTA), which perform the function of hole-transport layers [14, 15]), to the region of the emitter 4-CzPyCl4. Electrons from the metal cathode Ca:Al are injected into the same region through the LUMO (lowest vacant molecular orbital) electron transport layer of the compound 1,3,5-tris (n-phenylbenzimidazol-2-yl) benzene (TPBI) [16]. In this way, excitons are formed in the emitter layer, the annihilation of which leads to the formation of excited states belonging to both singlet and triplet states due to the intramolecular TADF of the 4-CzPyCl4 molecule [11]. A thin layer of diphenyl [4-(triphenylsilyl) phenyl] phosphine oxide (TSPO1) [17], was used in the structure to block excitons, thereby reducing the absorption of triplet excitons in the electron transport layer TPBI.

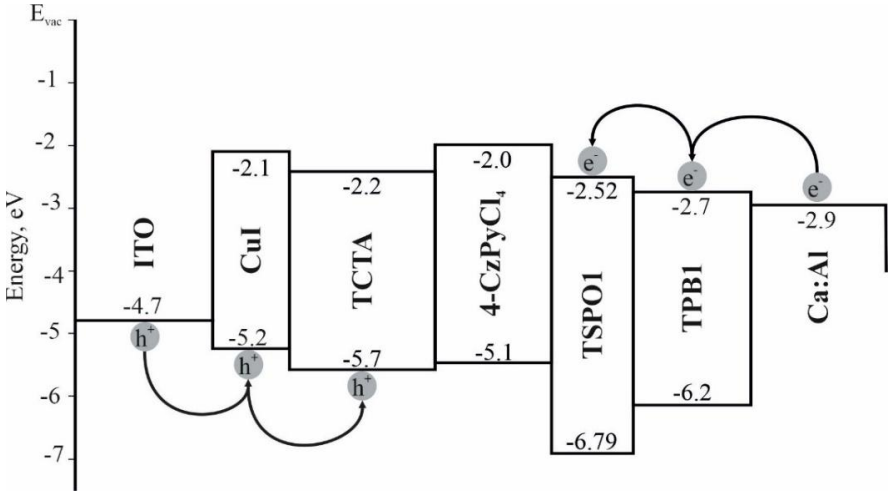

Fig. 3. Energy zone of the structure ITO/CuI/TCTA/4-CzPyCl4/TSPO1/TPBI/Ca/Al with the energy position of the levels of the constituent materials of OLED

3. Electroluminescent properties of the developed OLED structure

The electroluminescence spectrum ITO/CuI/TCTA/4-CzPyCl4/TSPO1/TPBI/Ca/Al is characterized by an emission maximum – a weakly expressed arm in the range of 440 nm, which slightly expands in the short-wavelength range relative to the photoluminescence spectrum of the 4-CzPyCl4 film (Fig. 4), which may be due to low emissions of TCTA – 385 nm [15] and TPBI – 370 nm [16] on the electroluminescence spectrum of OLED structure. However, the small high-energy radiation arm does not significantly affect the efficiency of the choice of transport layers for charge transfer in the structure. The electroluminescence spectrum of the OLED structure is quite similar to the photoluminescence spectrum of the 4-CzPyCl4 film, so it can be argued that it is responsible for OLED radiation.

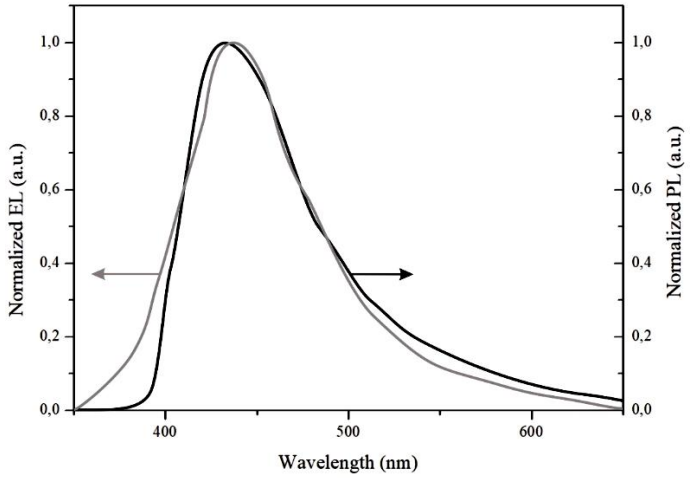

Fig. 4. Normalized electroluminescence spectra of OLED photoluminescence structure [11] of 4-CzPyCl4 solid film

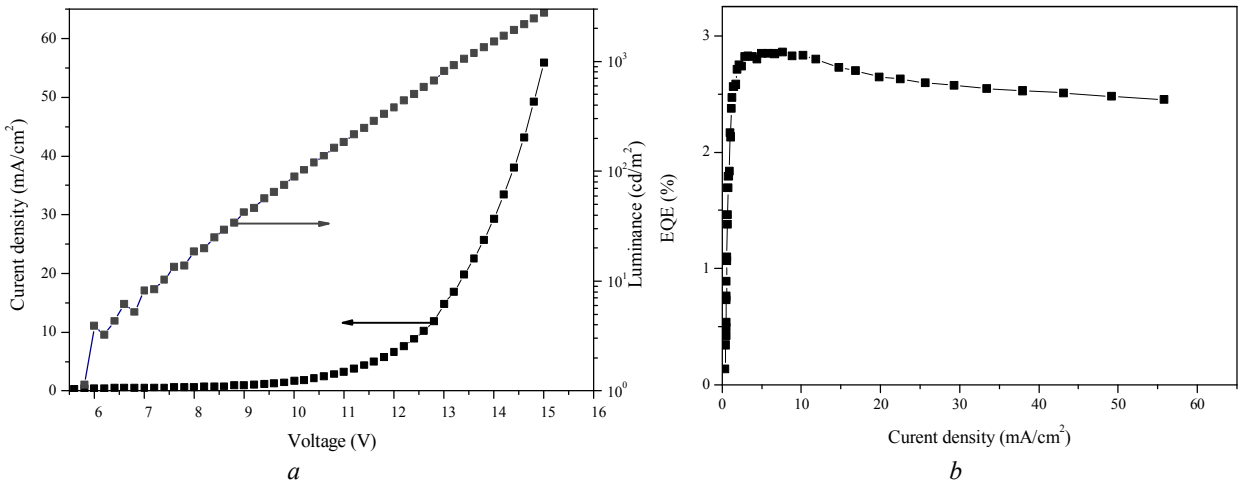

Fig. 5. Volt-ampere and brightness characteristics (a) and the dependence of the external quantum efficiency on the current density (b)

As can be seen from Fig. 5, *a*, after applying a bias voltage of 7.5 V to the organic heterostructure, the brightness of the device is 10 cd/m^2, and the value of the maximum brightness for bias voltages of 15 V exceeds 3000 cd/m^2. The OLED structure is characterized by an external quantum efficiency of 2.8 %. A characteristic feature of the light-emitting structure is the stability of the external quantum efficiency values (Fig. 5, *b*) at a wide range of current density values.

Chromaticity coordinates CIE(x,y) 1931 for the developed OLED structure are (0.15; 0.13), which corresponds to the "dark blue" spectral zone. Simultaneously we note that the increase of the current density to 55 mA/cm^2 does not lead to electroluminescence spectrum change, which also indicates good stability of the developed OLED. Finally, we note that significant increase of the quantum efficiency of OLED based on dark blue emitters requires introduction of a "guest-host" configuration to the OLED architecture [18]. The implementation of this approach increases the number of involved excitons formed in OLED, but the problem of selection of the "host" compound is still relevant, especially for dark blue emitters. In the future, the problem can be solved using OLED in the design of which the "host" is absent, and the radiating layer consists only of the emitter material, as in our case. Unfortunately, the use of a material without a "host" component for the manufacture of dark blue TADF emitters usually shifts the radiation spectrum to the long-wavelength range [19, 20]. We should note, however, that the developed OLED, despite the mediocre characteristics as for TADF OLED, did not show a significant shift in the long-wavelength region of the spectrum. Therefore, we believe that this promising result will help in the future to realize high-performance dark blue OLED without a guest-host combination.

4. Schematic implementation of the driver

In addition, development of the concept of a new generation of intelligent WOLED controllers [21], which in relation to known solutions was performed. The device are characterized by reduced power consumption and increased speed of periodic or continuous measurement of electrical characteristics, color coordinates and color index of WOLED structures. On the basis of such measurements it is possible to predict the drift characteristics of organic light-emitting structures during their operation for the prompt correction of their power regimes.

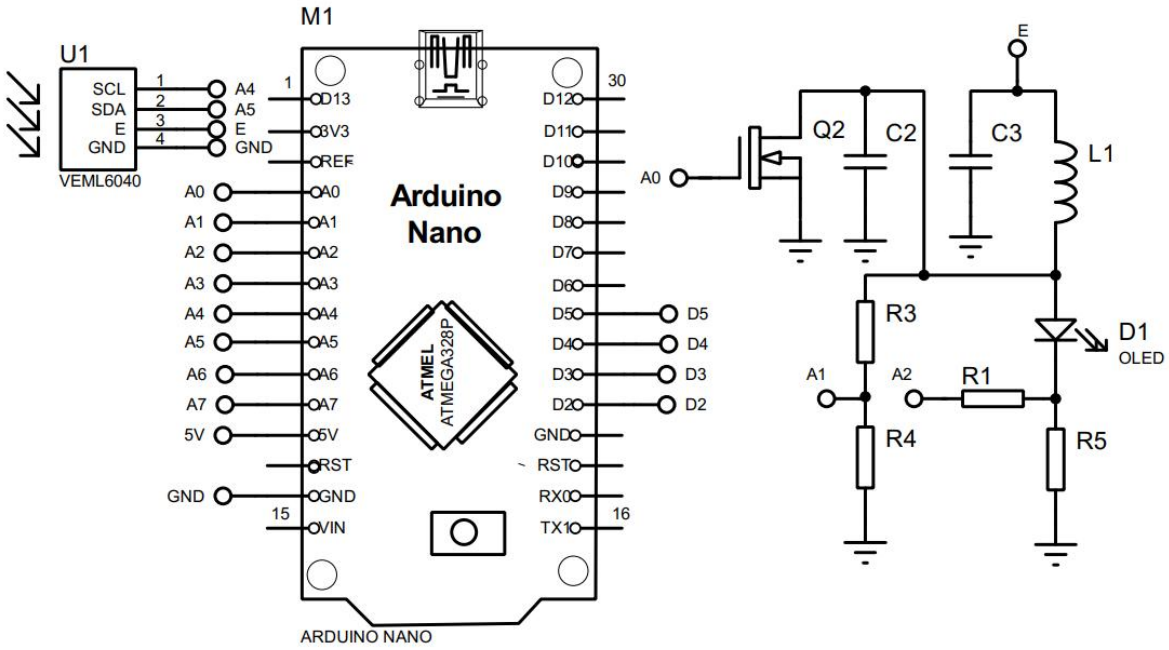

Fig. 6. Block diagram of the OLED driver based on a microcontroller (Color Light-to-Digital Converter)

In accordance with these requirements, the task of developing a new generation of controllers for the OLED structures is relevant. The novelty of this task is the integration of several functions in controllers, namely:

- controlled power supply of OLED structures with voltage increase on the principle of pulse boost drivers;
- study of the drift characteristics of OLED structures directly during their operation (such solutions use the term – "in-situ", which literally means "inside" the body or system);
- multi-mode measurement of CV characteristics of OLED structures using transient processes of voltage generation in driver boost circuits (such solutions use the term "boost", which literally means rapid increase);

measurement of color temperature of radiation of OLED structures directly during their operation, and such measurement should not be followed by considerable complication of the controller.Control of the power supply mode is provided by transistor T1, and control of the OLED current of the structure when measuring its CV characteristics is provided by transistor T2. Resistors R1, R2, R3, R4 form dividers, the output voltages of which are normalized to the range of analog-to-digital conversion. These dividers are fundamentally important, because the voltages on the OLED exceed the supply voltage of the microcontroller. Therefore, without dividers, the values of the measured voltages on the OLED not only go beyond the conversion range of the ADC, but can also lead to the failure of the entire signal conversion circuit [22].

The receiving module is based on the light-digital converter VEML6040 (Vishay). It consists of separate optical transducers for the red, green, blue and general (white) spectrum. The main optical characteristics of the module are shown in Fig. 7, and the functional diagram in Fig. 7.

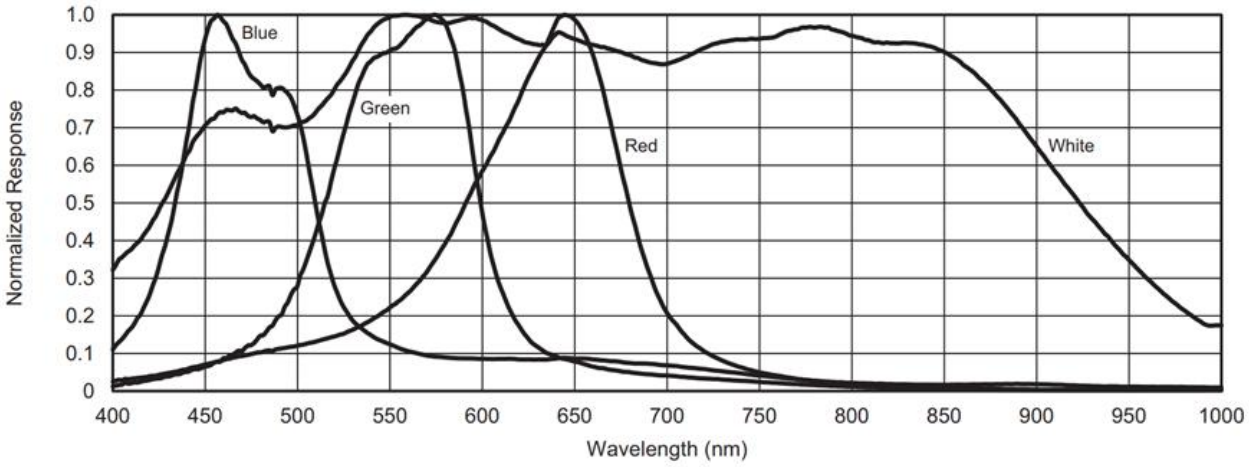

Fig. 7. Basic optical characteristics of the VEML6040 converter (Vishay)

There are other applications of controller units, in particular use of an amplifier with a programmable coefficient, which allows you to expand the ranges of measured voltages and programmatically control these ranges. A simple application involves the absence of negative current feedback, and therefore the absence in the circuit of transistor T2 and resistor R5 [23].

References

[1] *G. Schwartz, M. Pfeiffer, S. Reineke, K. Walzer and K. Leo. Adv. Mater (2007), Harvesting Triplet Excitons from Fluorescent Blue Emitters in White Organic Light-Emitting Diodes, (19), 3672–3676.*

[2] *ENERGY STAR Requirements for SSL Luminaires, Version1.1, ENERGY STAR requirements for integral LED lamps,U.S. Department of Energy, (2007).*

[3] *C. W. Han, W. Tak and B. C. Ahn J. (2007), Society information display.(19), 190–195.*

[4] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi (2012), Nature, Highly efficient organic light-emitting diodes from delayed fluorescence , (492), 234–238.

[5] G. Schwartz, S. Reineke, K. Walzer and K. Leo. (2008) Reduced efficiency roll-off in high-efficiency hybrid white organic light-emitting diodes Appl. Phys. Lett., (92).

[6] H. Sasabe, J. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido (2010), High-Efficiency Blue and White Organic Light-Emitting Devices Incorporating a Blue Iridium Carbene Complex, Adv.Mater.(22), 5003–5007.

[7] Y. Im, M. Kim, Y. J. Cho, J.-A. Seo, K. S. Yook, J. Y. Lee (2017), Molecular Design Strategy of Organic Thermally Activated Delayed Fluorescence Emitters, Chem. Mate (29), 1946–1963.

[8] Y. Seino, S. Inomata, H. Sasabe, Y. Pu, J. Kido (2016), High-Performance Green OLEDs Using Thermally Activated Delayed Fluorescence with a Power Efficiency of over 100 lm W-1, Adv. Mater. (28), 2638–2643.

[9] Organic electronics: a textbook / G. V. Baryshnikov, D. Yu. Volyniuk, I. I. Helzhinsky [etc.]; for ed. Z. Yu. Gotri. Lviv: Lviv Polytechnic Publishing House, 2019. 292 p.

[10] L.-S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani, and C. Adachi (2016), Controlling Singlet-Triplet Energy Splitting for Deep-Blue Thermally Activated Delayed Fluorescence Emitters, Appl. Chem. (56), 1571–1575.

[11] Y. Danyliv, R. Lytvyn, D. Volyniuk, I. Hladka, J. V. Grazulevicius (2018), Derivatives of carbazole and chloropyridine exhibiting aggregation induced emission enhancement and deep-blue delayed fluorescence, Dyes and Pigments, (149), 588–596.

[12] Elements and devices of organic electronics: a collective monograph / G. V. Baryshnikov, I. I. Gelzhinsky, Z. Yu. Gotra, H. B. Ivanyuk, B. P. Minaev, P. Y. Stakhira. Lviv: Space-M, 2020. 224 p.

[13] Organic light-emitting structures: collective monograph / G. V. Baryshnikov, I. I. Gelzhinsky, Z. Yu. Gotra, H. B. Ivanyuk, B. P. Minaev, P. Y. Stakhira. Lviv: Lviv Polytechnic Publishing House, 2020. 236 p.

[14] P. Y. Stakhira, V. V. Cherpak (2009), The properties of heterojunction based on CuI/pentacene/Al, Vacuum, 83 (8), 1129–113.

[15] I. Hladka, R. Lytvyn, D. Volyniuk, D. Gudeika, J. V. Grazulevicius (2018), W-shaped bipolar derivatives of carbazole and oxadiazole with high triplet energies for electroluminescent devices, Dyes and Pigments (149), 812–821.

[16] X. Tan, D. Volyniuk, T. Matulaitis, J. Keruckas, K. Ivaniuk, I. Helzhynskyy, P. Stakhira, J. V. Grazulevicius (2020), High triplet energy materials for efficient exciplex-based and full-TADF-based white OLEDs, Dyes and Pigments (177), 108259.

[17] Y. Danyliv, D. Volyniuk, O. Bezvikonnyi, I. Hladka, K. Ivaniuk, I. Helzhynskyy, P. Stakhira, A. Tomkeviciene, L. Skhirtladze, J. V. Grazulevicius (2020), Through-space charge transfer in luminophore based on phenyl-linked carbazole- and phthalimide moieties utilized in cyan-emitting OLEDs, Dyes and Pigments (172), 107833.

[18] S. H. Eom, Y. Zheng, E. Wrzesniewski, J. Lee , N. Chopra, F. So and J. G. Xue (2009), White phosphorescent organic light-emitting devices with dual triple-doped emissive layers, Appl. Phys. Lett. (94) 3.

[19] N. Aizawa, M. Numata, C. Adachi, T. Yasuda (2017), Versatile Molecular Functionalization for Inhibiting Concentration Quenching of Thermally Activated Delayed Fluorescence, Adv. Mater. (29), 1604856.

[20] Q. Zhang, D. Tsang, H. Kuwabara, Y. Hatae, B. Li, T. Takahashi, S. Y. Lee, T. Yasuda, C. Adachi (2015), Nearly 100 % Internal Quantum Efficiency in Undoped Electroluminescent Devices Employing Pure Organic Emitters, Adv. Mater. (27), 2096.

[21] G. Barylo, Helzhinsky I. I., Golyaka R. L., Marusenkova T. A., Khilchuk M. O. (2021), Built-in system of converter of supply voltage of organic light-emitting diodes, Bulletin of Khmelnytsky National University. No. 2 (295). pp. 151–155.

[22] G. I. Barylo, R. L. Holyaka, I. I. Helzhynskyy, Z. Yu. Hotra, M. S. Ivakh, R. L. Politanskyi (2020), Modeling of organic light emitting structures, Physics and Chemistry of Solid State Open Access, Vol. 21, Is. 3, pp. 519–524, 30 September 2020. DOI:10.15330/PCSS.21.3.519-524/

[23] G. Barylo, O. Boyko, I. Gelzynskyy, R. Holyaka, Z. Hotra, T. Marusenkova, M. Khilchuk, M. Michalska (2020), Hardware and software means for electronic components and sensors research, IAPGOŚ Informatyka, Automatyka, Pomiary W Gospodarce I Ochronie Środowiska. No. 10(1). pp. 66–71.

РОЗРОБЛЕННЯ НЕДОПОВАНОЇ ОРГАНІЧНОЇ СВІТЛОВИПРОМІНЮВАЛЬНОЇ СТРУКТУРИ ІЗ ЕМІСІЄЮ У ТЕМНО-СИНЬОМУ ДІАПАЗОНІ НА ОСНОВІ ДОНОРНО-АКЦЕПТОРНОГО МАТЕРІАЛУ КАРБАЗОЛОТЕТРАХЛОРОПІРИДИНУ

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Розроблення ефективних органічних світловипромінювальних діодів (OLED) на основі явища внутрішньомолекулярної термічно активованої уповільненої флуоресценції (TADF), у конструкції яких відсутні сині фосфоресцентні емітери на основі рідкоземельних металів, все ще залишається складним завданням галузі розроблення новітніх систем освітлення та OLED дисплеїв. У статті запропоновано технологічний підхід до формування такого типу OLED, емітером у якому є органічний донорно-акцепторний молекулярний матеріал 9-(2,3,5,6-тетрахлоропіридин-4-іл)-9H-карбазол (4-CzPyCl4), у якому електронна взаємодія між донорним і акцепторним фрагментами відіграє ключову роль у механізмі уповільненої флуоресценції. У конструкції розробленої світловипромінювальної гетероструктури використано пошарове формування функціональних нанорозмірних органічних плівок, на відміну від традиційних конструкцій OLED темно-синього кольору випромінювання, в яких застосовується система гість – господар. Зовнішня квантова ефективність розробленого OLED становить 2,8 %. Максимальна яскравість 3 000 кд/м^2 досягається за напруги 15 В. Координати колірності CIE(x, y) 1931 становлять (0,15; 0,13), що відповідає зоні темно-синього кольору.

Ключові слова: *OLED; уповільнена флуоресценція; екситон; електролюмінесценція; триплетні стани; зовнішня квантова ефективність.*