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CONTRIBUTION OF FLUORESCENCE AND EXCIPLEX EMISSION INTO VOLTAGE-DEPENDENT WHITE OLED

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Abstract. In this paper, the authors present the ability to control a white organic light-emitting diode's (WOLED) color temperature and radiation intensity. The architecture is proposed and a WOLED structure is developed based on the host-guest system. The function of the guest component is performed by a red ambipolar fluorescent emitter based on quinoxaline (CTQTC), and the host material is mCP (donor component of the exciplex mCBP: PO-T2T). Electroluminescence recombination occurred on the blue exciplex/electroplex mCP-PO-T2T and the guest CTQTC emitter. The emission intensity of the CTQTC emitter does not depend on the applied voltage, unlike the other bands of the emission spectra. The additional WOLED emission maximum is in the spectrum's green region due to the electrometric nature of the TAPC hole transport layer. The color temperature of the developed WOLED varied from 3000 to 4000 K in the applied voltage range from 8 to 14 V, corresponding to warm and cold white color. The device also exhibits a maximum brightness of 2968 cd/m^2 and a maximum external quantum efficiency of 4.07%.

Keywords: WOLED, exciplex, host-guest system, multilayer structure
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1. Introduction

Progress in modern lighting systems technologies and the appearance of modern displays on the market are largely due to the active replacement of traditional power sources with lighting systems based on organic fluorescent structures of white emission (WOLED) [1, 2, 3]. Low energy consumption, the possibility of forming on flexible substrates, and the absence of harmful substances in the design contributed to the successful commercialization of WOLED. It should be noted that the electroluminescent spectrum of WOLED is close to the spectrum of solar radiation, which makes WOLED a priority source of illumination when designing lighting control systems in a smart home. Note that the main purpose of automating the control system in such a building is to develop and improve maintenance and control assistance to improve the quality of services and the comfort of the residents. Depending on the geographical location and additional environmental parameters, the smart home management system must automatically optimize the color temperature and brightness level of the lighting systems and, as follows, maintain a comfortable state of human health to achieve better indicators during the rest period and productivity during the working period [4]. Notably, the light shade of sunset, dominated by orange and red colors, with a slight intensity of blue radiation, has a calming effect on the psychological and functional state. This is confirmed by a significant number of medical findings indicating a decrease in the inhibition of melanin secretion. The most important function of melanin is

antioxidant activity when illuminated with a low intensity of blue emission in the spectrum of white radiation [5]. At the same time, to ensure comfortable working conditions, it is desirable to use light with a spectrum close to white by standard CIE 1931. Therefore, the color parameters of WOLED radiation in the room require a specially adapted brightness and color temperature controller to achieve full functionality in lighting control [4]. It is worth noting that Warm-WOLEDs are light sources that exhibit a twilight shade with a color temperature ranging from 1500 to 3000 K. The color temperature of WOLEDs is in the range of 5000-6500 K, which is close to daylight [6]. Color temperature is a numerical value for determining the color of radiation from warm to cold, equivalent to the temperature of a completely black body, at which it emits light with the same chromaticity [7].

There are various approaches to forming WOLEDs; however, commercially successful ones usually contain organic donor-acceptor intermolecular exciplex complexes in their architecture as an effective emitters [8, 9]. Exciplex is characterized by thermally activated delayed fluorescence (TADF). In this case, the thermal energy (for example, that corresponds to room temperature) is sufficient to activate the reverse intersystem crossing (RISC) in the narrow energy gap between the triplet and singlet excited states [10-13]. The following relaxation of the excited molecule to the ground state can be accompanied by highly efficient TADF radiation.

The actual difference between such long-term fluorescent radiation and typical fast fluorescence is that before the emission of light, the excited molecule is in the triplet state for some time. The internal quantum efficiency of WOLED can theoretically reach one hundred percent due to the realization of triplet-singlet interaction in the case of TADF in the device. Also, the exciplex is functionally able to perform the role of the energy state of charge transfer between the donor and acceptor molecules. This enables the implementation of an efficient WOLED with a simple structure by redistributing the energy of the triplet stage exciplex, the singlet stage exciplex, and the fluorescent emitter [14]. The main advantages of exciplex are the relative simplicity of obtaining exciplex radiation by mixing donor and acceptor molecules in the solid state, as well as the possibility of using exciplex complexes as emitters and "host" components. It creates good prerequisites for the wide application of exciplexes in WOLED manufacturing technology [15-17]. It is possible to partially control the color temperature of the white organic light of the diode by the applied voltage in devices as a result of a combination of exciton and exciplex-electroplex emission [18]. In the paper, we report on design and technological solutions for obtaining a WOLED with the ability to control voltage-dependent color parameters.

2. Results and discussion

The most widely used method for fabricating exciplex-based WOLEDs is to combine the blue exciplex emission with complementary exciplex emissions, such as green/red exciplex emissions. To get white electroluminescence by mixing blue and orange emissions, multicolor exciplex and electroplex emissions are an essential requirement for the new WOLED based on an RGB system. WOLED Structure: ITO/CuI(8 nm)/ m-MTDATA (20 nm)/TAPC(20 nm)/mCP: CTQTC (20 nm, 10%)/PO-T2T (30 nm)/Ca(50 nm)/Al(200 nm) (Fig. 1.)

The structure was formed by thermal deposition in a vacuum (10-5 Torr) on a glass substrate with a transparent conductive layer of indium tin oxide (ITO), by stepwise deposition of a hole-injection layer of CuI [19], two hole-transporting layers 4,4',4''-

Tris[phenyl(m-tolyl) amino]triphenylamine (m-MTDATA) [20] and 1,1-Bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) [21] along with electron-transporting layer 4,6-tris[3 (diphenyl phosphinyl) phenyl]-1,3,5-triazine (PO-T2T) [14]. Red ambipolar emitter based on quinoxaline (CTQTC) [22], doped in mCBP (3,3′-Di(9H-carbazol-9-yl)-1,1′-biphenyl)/PO-T2T exciplex ((4,6-tris[3 (diphenyl phosphinyl) phenyl]-1,3,5-triazine)) [1]. The mCBP: CTQTC matrix was formed by controlled simultaneous deposition from two sources. Calcium (Ca) and Aluminium (Al) were used as cathode materials with low work function, providing good electron injection to the electron-transport layer.

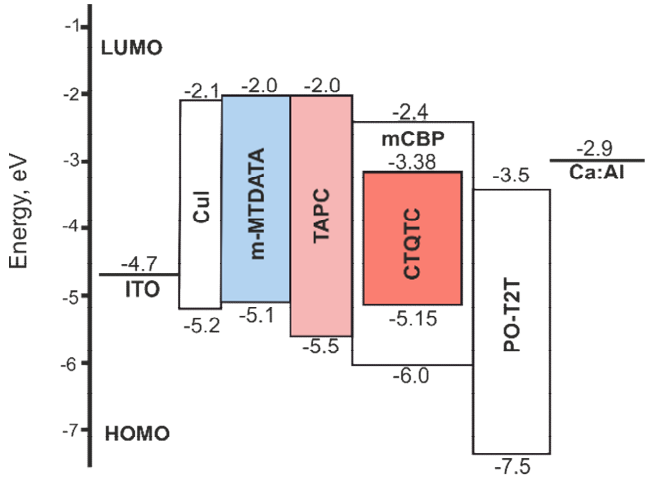

Fig. 1. Schematic diagram of the device architecture and energy positions of the HOMO and LUMO levels of the functional layers (HOMO is the highest occupied molecule orbital, and LUMO is the lowest unoccupied molecular orbital).

Additionally, the m-MTDATA layer has performed the function of a blue fluorescent emitter. The mCBP and PO-T2T layers were used as the donor and acceptor components of the exciplex, respectively [23].

Experimental dependencies of current density on voltage and brightness voltage were obtained using a semiconductor parameter analyzer (HP 4145 Å). All measurements were performed at room temperature in ambient conditions without passivation, immediately after forming the devices. Brightness was measured using a calibrated photodiode. Electroluminescence spectra were recorded with an Ocean Optics USB2000 spectrometer.

The electroluminescence spectra of the device are characterized by five different radiation bands superimposed. It varies depending on the applied voltage (Fig. 2a). The presence of bands is explained by the simultaneous light-emitting recombination of excited states of different natures. The device's emission, with the highest high energy around 425 nm, is characteristic of pure m-MTDATA fluorescence emission [24]. The presence of a band with a maximum value of 540 nm is explained by forming an electroplex of the TAPC layer [25]. The shoulder band of the WOLED electroluminescence with a peak value of 600 nm is close to the maximum value of the electroluminescence emission of the CTQTC emitter [22]. The structure of the developed device provides for the implementation of energy transfer to the red CTQTC emitter from the host of the exciplex mCBP: PO-T2T (Fig. 1). The method of "interface technology" which was used to fabrication device is similar to successfully implemented in the transfer of energy from an exciplex (matrix system) to a highly efficient fluorescent emitter by the authors of the work [14].

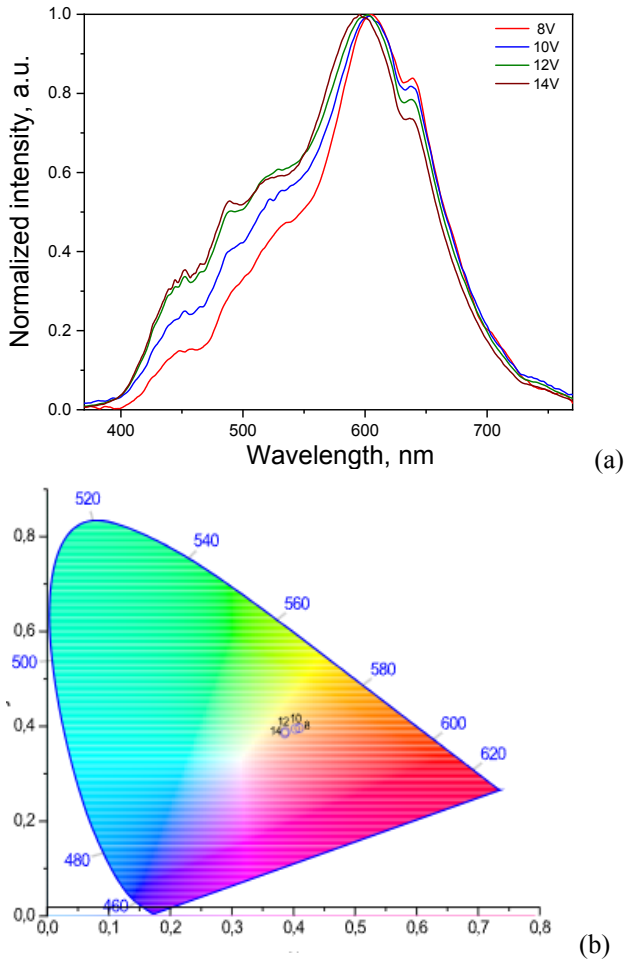

Fig. 2. Electroluminescence spectra of WOLED at different applied voltages(a) and a CIE1931 chrominance diagram of the device at voltages from 8 to 12 V(b). The device's color coordinates are shown as blue dots.

This approach involves diffusion of the CTQTC layer into the mCP matrix (the donor component of the exciplex mCBP: PO-T2T). At the same time, when an electric voltage is applied, electroluminescent recombination occurs both on the mCP - PO-T2T exciplex (470 nm) and on the guest CTQTC emitter, which indicates energy transfer between the exciplex host and CTQTC according to the Förster mechanism. The presence of a higher position of the energy singlet state of the exciplex S1 mCBP: PO-T2T (2.64 eV) over the first singlet state S1 of the CTQTC emitter (2.13 eV) is one of the main conditions for Förster energy transfer [22, 26]. The low-energy peak (640 nm) corresponds to the excimer/electromeric emission of the CTQTC material [22].

Fig. 2a shows electroluminescence spectra at different applied voltages. With an increase in the applied voltage from 8 to 14 V, we can observe that the main maximum of the emission shifts to the high-energy region from 606 to 594 nm. This continues while amplitude remains constant. Conversely, the maxima of the exciton bands (425 nm), exciplex radiation (470 nm), and electrometric emissions with maxima at 520 nm and 640 nm remain constant while their intensity increases. So, as the voltage increases, the color rendering quality of the device changes.

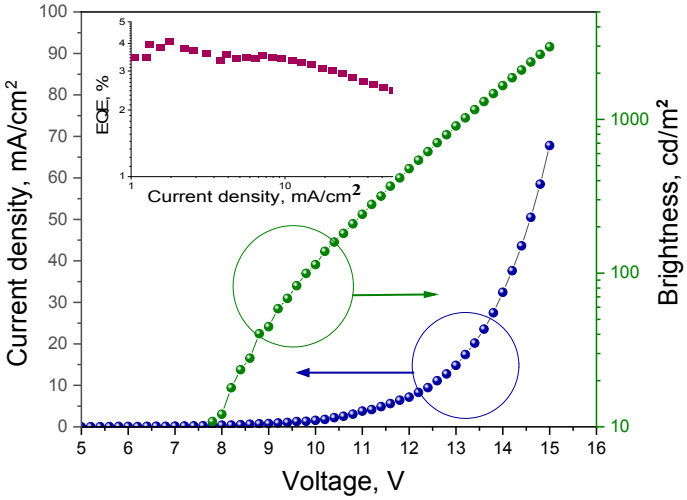

Fig. 3. Brightness–voltage-current density curves Inset: External quantum efficiency–current density of the device.

At the same time, the CIE 1931 coordinates change as follows (0.4394:0.409), (0.403:0.3948), (0.3867:0.3886), (0.3857:0.38538) (Fig. 2b) at a voltage of 8 V, 10 V, 12 V, 14 V, respectively. The color temperature of the corresponding electroluminescent spectra changes from 3000 to 4000 K (color temperature determination table) at different applied voltages.

The brightness–voltage-current density characteristics show a WOLED turn-on voltage value of 8 V, corresponding to electroluminescence of 10 cd/m^2. The device also demonstrates a maximum brightness of 2968 cd/m^2 (at 15 V) (Fig. 3). The maximum external quantum efficiency was 4.07% at 9 V.

3. Conclusions

We demonstrate an approach to the realization of a WOLED structure based on the combination of different types of emission. In the device implemented, the energy redistribution of the blue mCBP: PO-T2T exciplex and the red fluorescent emitter and the use of electroplex emission. The non-resonant energy transfer from the exciplex's singlet state to the CTQTC doping impurity according to the Förster mechanism and the presence of electroplex emission to WOLED efficiency. The presence of voltage-dependent excited states of the exciplex and electroplex type allows for redistribution of the spectral composition of the device's electroluminescence. The device thus developed can be used to adjust the white emission from warm to cold by changing the WOLED supply voltage. This concept is desirable because today's smartphone displays already use a change in color temperature (so-called "night mode"). This is also in demand for future indoor lighting applications. So far, this can only be realized by combining multiple WOLEDs of different colors and not in a single device.

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Анотація. *У цій статті автори представляють можливість керувати колірною температурою та інтенсивністю випромінювання білого органічного світлодіода (WOLED). Пропонується архітектура та розробляється структура WOLED на основі системи господар-гість. Функцію гість-компоненти виконує червоний амбіполярний флуоресцентний емісійний матеріал на основі хіноксаліну (CTQTC), а матеріалом-господарем є mCP (донорна компонента екциплексу mCBP: PO-T2T). Електролюмінесцентна рекомбінація відбулася на синьому екциплексі/електроплексі mCP-PO-T2T і гостьовому випромінювачі CTQTC. Інтенсивність випромінювання випромінювача CTQTC не залежить від прикладеної напруги, на відміну від інших смуг спектрів випромінювання. Додатковий максимум випромінювання WOLED знаходиться в зеленій області спектра через електрометричну природу транспортного шару дірок TAPC. Колірна температура розробленого WOLED варіювалася від 3000 до 4000 K в діапазоні прикладеної напруги від 8 до 14 В, що відповідає теплому і холодному білому кольору. Пристрій також демонструє максимальну яскравість 2968 кд/м² і максимальну зовнішню квантову ефективність 4,07%.*

Ключові слова: *WOLED, exciplex, host-guest system, multilayer structure*