



REGULAR ARTICLE

The Quantum Efficiency Roll-off-free Red Organic Light-emitting Diode via Quantum Well Structure

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Technology for fabricating red organic light-emitting diodes (OLEDs) based on a multiple quantum well (MQW) structure is considered. The study aimed to develop an OLED using the MQW structure to prevent the quantum efficiency roll-off at high operating voltages, a common issue in traditional OLEDs that use doped host-guest systems. Two OLED types were fabricated to achieve this: one with a doped host-guest system and another with an MQW structure. The electrical characteristics of both devices were compared in this research, focusing on quantum efficiency. A narrow-band orange organic emitter with thermally activated delayed fluorescence emission (TADF) 2,3,5,6-tetrakis(3,6-diphenyl-9H-carbazol-9-yl)-1,4-benzenedicarbonitrile (4CzTPN-Ph) was used for the new structure, sandwiched between two layers of wide-band semiconductor mCBP, creating a quasi-two-dimensional (2D) heterostructure. Implementing the MQW structure significantly reduced the quantum efficiency roll-off at higher voltages, offering a major advantage over traditional OLEDs, where such roll-off often leads to performance reduction and shortened device lifetimes. The results showed that the OLED with the MQW structure demonstrated a brightness exceeding 600 cd/m², and stable quantum efficiency across the entire operating voltage range. Unlike traditional OLEDs, where doped systems often face challenges with uneven charge and energy distribution, the MQW structure enables better exciton confinement and more efficient utilization, thus improving device stability. Furthermore, using the MQW structure allowed for enhancement of the colour characteristics of OLEDs, making them more saturated and accurate, which is important for commercial applications such as displays and lighting systems.

Keywords: Organic light emitting diode, Quantum wells, Efficiency, Heterostructure, Brightness, Exciton.

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1. INTRODUCTION

Light-emitting diode (LED) technology dominates the lighting industry, largely due to the numerous initiatives to replace outdated lighting systems reliant on incandescent bulbs. This transition is driven by the demand for enhanced energy efficiency, which, in solid-state lighting technology, is up to ten times greater thanks to the direct energy conversion phenomenon of electroluminescence. LED technology offers high-quality illumination, providing the flexibility to adjust the luminous flux, compact dimensions, and economic advantages, including an extended life cycle [1]. Meanwhile, significant advancements in organic materials have paved the way for introducing a new lighting technology: organic light emitting diodes (OLEDs) [2]. Enhancement in applications and the miniaturization of electronics has led to the exploration of many advanced materials including quantum dots, organic molecules, carbon nanotubes, nanowires, and single atoms or molecules [3]. One of the key innovations is the use of quantum dots, which have unique electronic and optical properties, in particular, the ability to emit light of different colours depending on their size [4]. Quantum dots can be integrated into OLEDs to improve colour performance and stability. However, one of the

negative aspects of using quantum dots is that they often contain toxic and rare metals such as cadmium, selenium, lead, zinc, indium, tellurium, and other heavy metals.

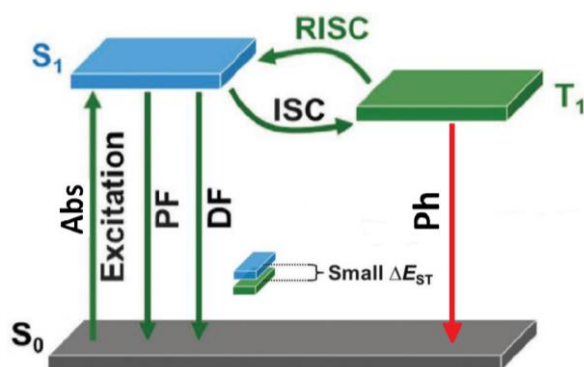
As mentioned, the main operational requirements for OLED are to increase luminous efficiency, brightness, reliability and reduce costs. Thus, the OLED power efficiency has been improved continuously since the first introduction of this technology. To date, OLED technologies have been divided into several generations, depending on the characteristics of the emitter, which determine the properties of the diode constructed with its use. The main differences between them can be explained using quantum mechanics. In an OLED, the electrical current leads to an excitation of the molecules and thereby to the creation of singlet and triplet excitons. The energies of the singlet exciton are higher than those of the triplet excitons, but for every singlet exciton, three triplet excitons are generated. The internal quantum efficiency (IQE) of OLEDs using first generation fluorescent materials is limited to 25 % for the reason that the emitter can only harvest singlet excitons according to spin statistics [5, 6]. Second generation phosphorescent materials containing noble metal atoms can fully utilize both singlet and triplet excitons

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through effective spin-orbital coupling achieving IQE $\sim 100\%$ which achieves maximum external quantum efficiency (EQE) of up to 30% with extremely low efficiency roll-off depending on the operating time [7]. However, this requires the use of expensive rare and rare earth metals. It is also necessary to emphasize the complexity of the process of synthesizing phosphorescent materials [8, 9].

To overcome the existing limitations, in 2012 Japanese researchers presented the third generation OLED using an organic thermally activated delayed fluorescence molecule as an emitter [10]. TADF materials provide high stability and a wide range of colours, have a much simpler synthesis scheme, expanded selective components making them extremely promising for the production of efficient OLEDs. TADF emitters can increase the OLEDs efficiency due to their ability to convert triplet excitons to singlet ones, which allows for nearly 100% internal quantum efficiency without using expensive rare metals such as iridium, cadmium, and molybdenum [11]. Their feature is that for efficient TADF molecules, a sufficiently small energy gap (ΔE_{ST}) between the singlet (S_1) and triplet (T_1) states is desired to facilitate the reverse intersystem crossing (RISC) process. Theoretically, the ΔE_{ST} value can be minimized by controlling the separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) through molecular design [12]. Therefore, TADF is often observed in intramolecular-charge-transfer (ICT) systems containing spatially separated donor (D) and acceptor (A) moieties. Fig. 1 shows a model to describe reverse intersystem crossing in donor-acceptor charge transfer molecules. This mechanism describes the basic photophysics of TADF. Knowing the underlying photophysics of thermally activated delayed fluorescence allows proper design of high efficiency organic light-emitting diodes [13].



* Abs – Absorption; PF – Prompt Fluorescence ($\tau \approx \text{ns}$); DF – Delayed Fluorescence ($\tau \approx \mu\text{s}$); Ph – Phosphorescence ($\tau \approx \text{ms}$); ΔE_{ST} – Energy splitting of S_1 & T_1

Fig. 1 – Mechanism for using TADF emitters in electroluminescence application

One of the main challenges of this technology remains the low efficiency of NIR/red OLEDs [14] due to triplet quenching, which occurs due to triplet-triplet annihilation [15], as well as the complexity of the synthesis of stable red emitters, as achieving both a small ΔE_{ST} value and a high fluorescence rate (k_F) within a single molecule is difficult due to molecular design con-

straints. A small ΔE_{ST} , which is necessary for efficient TADF, usually results in reduced orbital overlap, leading to a lower k_F , which negatively affects photoluminescence efficiency (Φ_{PL}) because of increased non-radiative transitions [16]. Different TADF approaches have been then employed to increase the efficiency of fluorescent OLEDs including TADF emitting molecules, TADF assistant dopant molecules, TADF exciplex hosts, or several different combinations of them (exciplexes, host-guest systems, etc.) [17].

However, despite significant advances in this field, red OLEDs still face critical challenges, particularly the considerable quantum efficiency roll-off at high operating voltages, characteristic of traditional designs using doped host-guest systems. Compared to other colours, the design and synthesis of efficient red emitters is more complicated, corresponding to the energy gap law [15]. Many red emitters suffer from a poor compromise between device efficiency and colour purity. The lower brightness of the red device is due to its characteristic red radiation in the spectral emission where the eye has low sensitivity. Moreover, the wide bandgap host used in OLED devices and the narrow bandgap red-emitting guest have a significant difference in the HOMO and/or LUMO levels between the guest and host materials. Thus, the guest molecules are believed to act as deep traps for electrons and holes in the emissive layer, causing an increase in the driving voltage of the device. Furthermore, self-quenching or triplet-triplet annihilation for red dopant molecules is an inevitable problem in such host-guest systems, especially at high doping concentrations [18]. Therefore, from a practical standpoint, a solution to the above problems based on material design and device optimization is highly desirable.

An effective solution for improving the technology of red OLEDs, which does not require the procedure of doping the emitter into the matrix material, was the introduction of semiconductor MQW structures into their design, which are a 2D-heterostructure in which a thin semiconductor layer with a narrower band gap is sandwiched between two semiconductors with a wide bandgap in such a way as to provide dimensional quantization of the electronic levels [19]. These structures allow optimization of the interaction between excitons and materials, leading to improved stability and improved device performance. MQWs provide more effective exciton containment, preventing rapid decay at high operating voltages. The use of MQW structures also makes it possible to significantly reduce the drop in quantum efficiency, which is characteristic of traditional OLEDs.

Thus, this research is aimed at the development and fabrication of red OLEDs based on a combination of TADF and MQW technologies. The goal of the work is to achieve high brightness and stable performance of devices in a wide range of voltages. In particular, the combination of an orange donor-acceptor TADF emitter, such as 4CzTPN-Ph, with MQW structures makes it possible to create red OLED that exhibits not only high brightness but also resistance to quantum efficiency roll-off due to quantum limitations [20]. The results of this research can become the basis for devel-

oping efficient and reliable red OLEDs that meet the requirements of modern industry.

2. METHOD AND MATERIALS

All materials were obtained commercially and used directly without further purification.

Organic semiconductor functional layers and metal electrodes were deposited under a vacuum of around 2×10^{-6} mbar using UVR-3M serial vacuum equipment for the thermovacuum deposition of thin films by the method of controlled co-deposition from two crucibles. The speed and thickness of deposited materials were controlled with the help of quartz resonators built into the working chamber of the UVR-3M. The change in frequency was recorded using frequency meter ChZ-34A. The thickness measurement is based on deviations of the resonant frequency of a quartz crystal resonator caused by a change in the quartz plate mass. As the plate mass of the mechanical resonator increases due to the deposition of matter on its surface, the resonant frequency shifts [21].

Dependence between frequency shift $\Delta\omega$ and mass change Δm quartz resonator is described by the following Equation 1:

$$\frac{\Delta\omega}{\omega_0} = \frac{\Delta m}{m_0} \quad (1)$$

The film thickness h was determined by the formula 2 [21]:

$$h = \frac{\Delta\omega m_0}{\omega_0 S \rho} \quad (2)$$

where Δm is the mass of the deposited film, ρ is its density, and S is the area occupied by the film on the quartz plate.

For OLED fabricating, the pre-patterned indium-tin oxide (ITO)-coated glass substrates with seven pixels of a 6 mm², precleaned with isopropyl alcohol and acetone in an ultrasonic bath for 15 minutes were used. The current density, voltage, and brightness characteristics were measured using a source meter HP4145A and the method of calculating brightness characteristics. The brightness measurement was obtained using a calibrated photodiode, and the Ocean Optics USB2000 spectrometer was used to record electroluminescence spectra. All devices were manufactured without additional sealing and tested immediately after forming the structures in the air at room temperature.

3. RESULTS AND DISCUSSION

The electroluminescent (EL) properties of both OLEDs with host-guest dopant system and MQW structure were studied using the following structures: reference organic light-emitting device, without quantum wells (Device A - ITO/CuI (5 nm)/TAPC (40nm)/mCBP: 4CzTPN-Ph (40 nm)/TSPO1 (10 nm)/TPBi (40 nm)/Ca (2 nm)/Al) with host-guest dopant system and OLED with quantum wells (Device B - with the structure ITO/CuI (5 nm)/TAPC (40 nm)/mCBP (15 nm)/ 4CzTPN-Ph (5 nm)/ mCBP (5 nm)/ 4CzTPN-Ph (5 nm)/ mCBP (5 nm)/ 4CzTPN- Ph (5 nm)/TSPO1 (10 nm)/TPBi (40

nm)/Ca (2 nm)/Al), respectively. The molecular structures of organic semiconductors used in the light-emitting functional layers for the fabrication of devices A and B are given in Fig. 2a, b. Fig. 2c shows the energy level diagram of devices A and B.

Indium tin oxide (ITO) was used as an anode material, Copper Iodide (CuI) as a hole-injection layer, 1,1-Bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) and diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSPO1) as a hole-transport layer and hole-blocking material, respectively. 2,2',2''-(1, 3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) was selected was used for the deposition of the electron-transporting layer

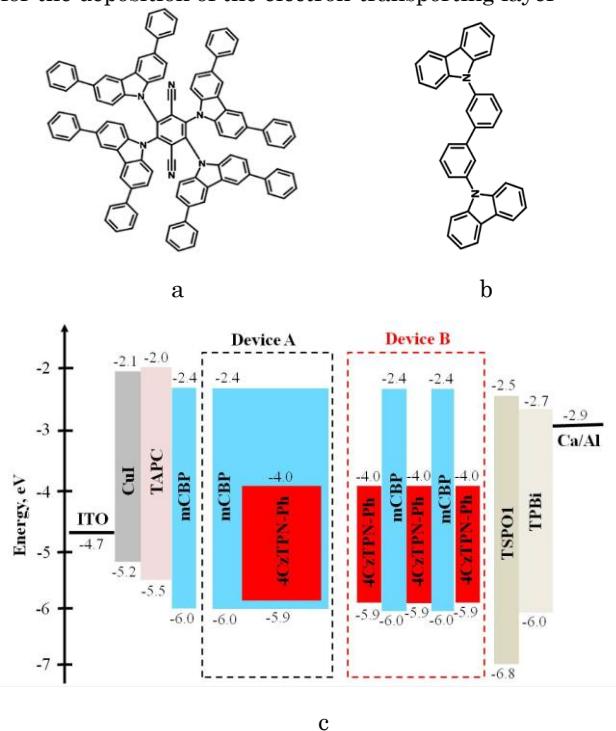


Fig. 2 – Chemical structures of 2,3,5,6-tetrakis(3,6-diphenyl-9H-carbazol-9-yl)-1,4-benzenedicarbonitrile (4CzTPN-Ph) (a), and 3,3'-Di(9H-carbazol-9-yl)-1,1'-biphenyl (mCBP) (b). Energy level diagram of doped (reference) OLED (Device A) and QW-OLED with a structure of quantum wells (Device B) (c)

which alleviates the stepwise electron transfer from the Ca:Al cathode to the emissive layer. The orange ambipolar emitter 2,3,5,6-tetrakis(3,6-diphenyl-9H-carbazol-9-yl)-1,4-benzenedicarbonitrile (4CzTPN-Ph) was doped into the matrix 3,3'-Di(9H-carbazol-9-yl)-1,1'-biphenyl (mCBP) by the method of controlled co-deposition from two crucibles in a ratio of 50:50.

As a host compound, mCBP in the structure of Device A was chosen due to its high-energy first triplet state, $T_1 = 2.91$ eV [22], which exceeds the $T_1 = 2.21$ eV value of the 4CzTPN-Ph emitter [23]. Such a combination prevents energy loss through the triplet levels of the matrix. Moreover, as can be seen from the Fig. 3a, inset, due to the low dipole moment of mCBP [24], the EL spectrum of Device A shifted toward the short-wavelength EL region with a peak at 612 nm compared to the photoluminescence spectrum of the 4CzTPN-Ph emitter thin film, the peak of which reached around 624 nm.

The main feature in the structure of Device B is the host-guest system absence, as well as a cascade of three

QWs ($n = 3$) presence, in the structure of which 4CzTPN-Ph ultrathin film was placed between the mCBP of the same type for the first and second QWs and between the mCBP and TSPO1 layers for the third QW.

Fig. 3 shows the main electrical characteristics of the manufactured devices, and their quantitative param-

eters are summarized in Table 1. Device A based on the host-guest dopant system with a 4CzTPN-Ph emitter shows a low turn-on voltage, and stable brightness characteristics in a wide range of current density (Fig. 3b). The EQE roll-off for Device A is negligible, probably due to balanced charge trapping in the emissive layer.

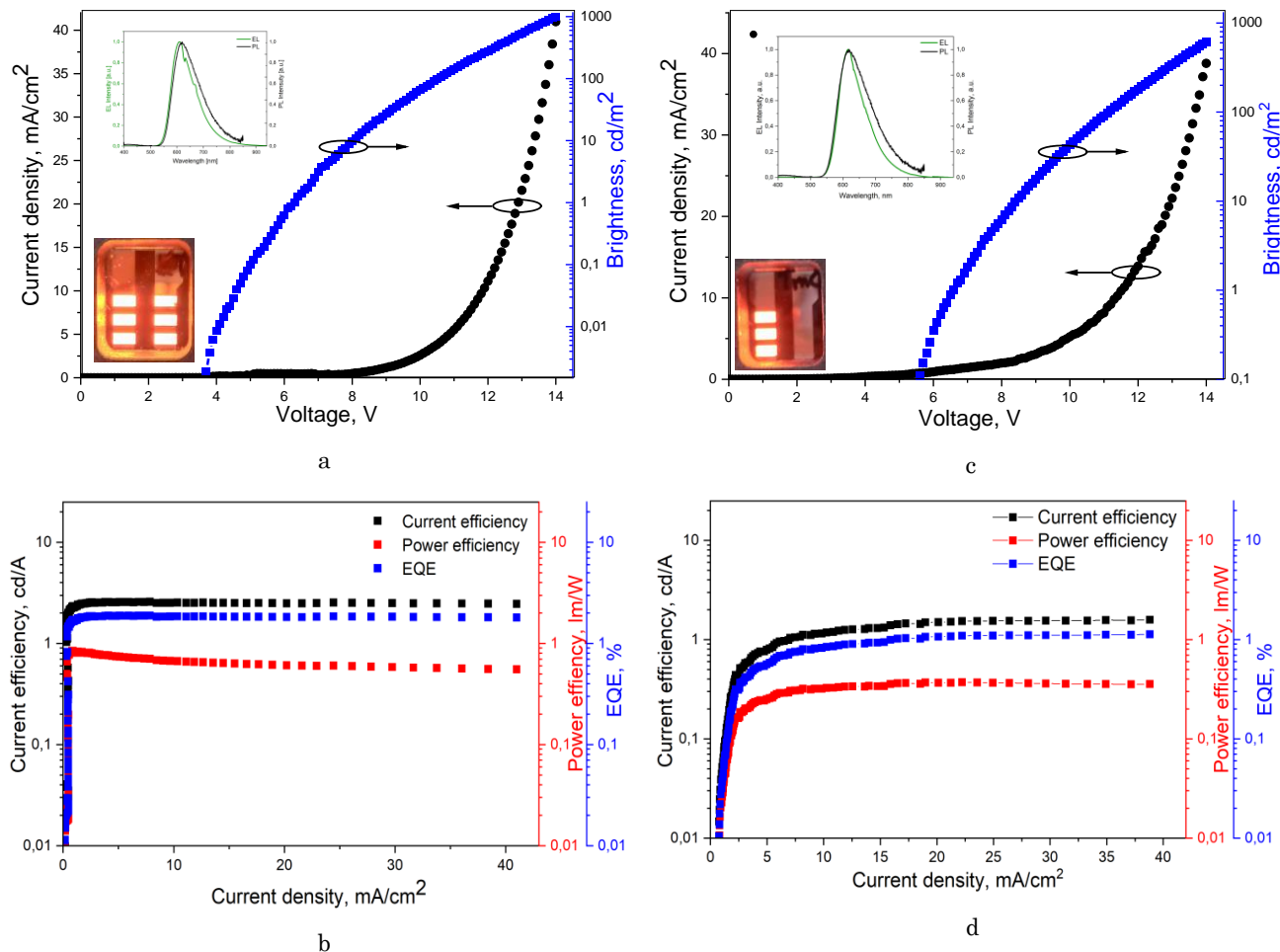


Fig. 3 – J - B - V characteristics of devices A (a) and B (c). (Inserts: The EL spectra vs. the thin film PL spectra of EML layers and the images of the fabricated devices A and B, respectively). CE (current efficiency), PE(power efficiency), and EQE (external quantum efficiency) versus current density plots of devices A (b) and B (d)

Table 1 – The EL performances of red reference OLED (Device A) and QW-OLED with a MQW structure (Device B)

Device	Turn-on voltage (V)	Maximum luminance (cd/m ²)	CE _{max} , ^a (cd/A)	PE _{max} , ^b (lm/W)	EQE _{max} , ^c (%)	CIE, ^d (x, y)
A	3.7	1012.15	2.60	0.85	1.90	(0.51, 0.38)
B	5.6	616.14	1.59	0.36	1.13	(0.54, 0.35)

^a CE_{max}: Maximum current efficiency. ^b PE_{max}: Maximum power efficiency. ^c EQE_{max}: Maximum external quantum efficiency. ^d CIE_{x,y}: Commission International de L'Eclairage coordinates at 10 mA cm⁻².

The electroluminescence spectra with peak emission at 618 nm and the photoluminescence spectra of the EML layer thin film with a maximum of 619 nm for Device B, (Fig. 3c, inset), provide its better light characteristics and demonstrate a significantly smaller shift of the EL spectrum to the short-wavelength region, compared to the EL spectrum Device A (Fig. 3a, inset), which is the main advantage for a device with an MQW structure. The colour coordinates (x, y) according to the Commission International de L'Eclairage (CIE) 1931

standard of Device B (0.54; 0.35) also show a higher purity of red colour, compared to their values for structure A (0.51; 0.38) (Fig. 4).

Thus, Device B is characterized by lower current consumption and a quantum efficiency roll-off absence, despite a slightly higher turn-on voltage and the lower EQE maximum compared to Device A (Table 1), which makes this device quite stable and reliable in operation (Fig. 3d).

4. CONCLUSIONS

To summarize, the development and electrical performance of red OLEDs, based on doped host-guest systems and MQW structures have been considered. QW-OLED obtained a brightness more of than 600 cd/m², and an external quantum efficiency of about 1.13 % at

14 V. Chromaticity coordinates CIE1931 of this device ($x = 0.54$, $y = 0.35$) correspond to the International Commission on Illumination coordinates for red OLEDs ($x \geq 0.60$, $y \leq 0.40$). The strategy of combining a narrow-band organic orange material with thermally

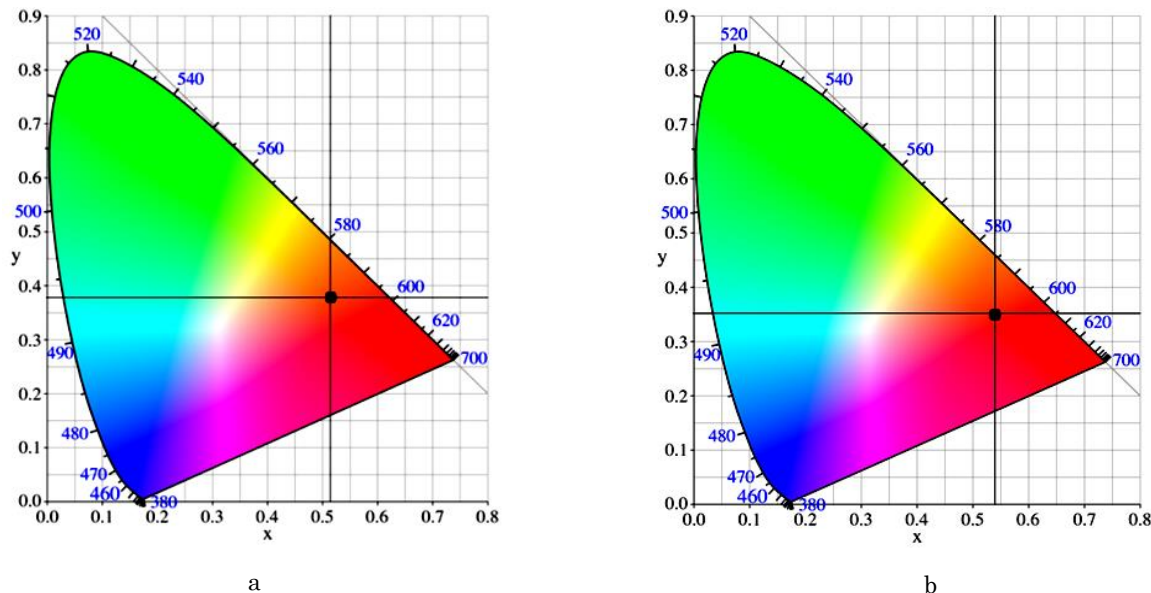


Fig. 4 – CIE 1931 chromaticity coordinates of devices A (a) and B (b)

activated delayed fluorescence in the fabrication of a red OLED with a quantum well structure without a quantum efficiency roll-off is important for preparing efficient and stable OLEDs. Thus, technologies using quantum wells in combination with TADF materials open up new opportunities for further improvement of organic LEDs, offering high efficiency, stability and a rich colour range. Especially promising is the combination of MQW and TADF, which provides improved characteristics compared to traditional OLEDs, which makes such devices attractive for the latest displays

and lighting systems. The use of quantum well structures also opens up new horizons for improving red OLEDs, increasing their performance and stability.

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Органічний світловипромінюючий діод з випромінюванням червоного кольору без спаду квантової ефективності із застосуванням технології «квантових ям»

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У роботі описано технологію виготовлення червоних органічних світлодіодів (OLED) на основі структури квантових ям (MQW). Метою дослідження було розробити OLED із застосуванням MQW для запобігання спаду квантової ефективності приладу при високих робочих напругах, що характерно для традиційних OLED, що використовують леговані системи типу "господар-гість". Для цього було виготовлено два типи OLED: з легуючою системою «господар-гість» і структурою MQW, відповідно. У дослідженні порівнювали електричні характеристики обох приладів, приділяючи особливу увагу квантовій ефективності. Для створення нової структури був використаний вузькозонний помаранчевий органічний емітер з термічно активованим уповільненим флуоресцентним випромінюванням (TADF) 2,3,5,6-тетракіс(3,6-дифеніл-9H-карбазол-9-іл)-1,4-бензолдикарбонітрил (4CzTPN-Ph), розміщений між двома шарами широкозонного напівпровідника mCBP, що дозволило створити квазідвовимірну гетероструктуру (2D). Завдяки впровадженню структури MQW вдалося суттєво знизити спад квантової ефективності при підвищенні напруги, що є значною перевагою в порівнянні з традиційними OLED, де такий спад часто призводить до погіршення продуктивності та зменшення терміну служби приладів. Результати дослідження показали, що OLED зі структурою квантових ям демонструє яскравість, що перевищує 600 кд/м², а також стабільну квантову ефективність протягом усього робочого діапазону напруг. На відміну від традиційних OLED, де леговані системи зазвичай стикаються з проблемою нерівномірного розподілу заряду та енергії, структура квантових ям сприяє кращому утриманню екситонів і ефективнішому їх використанню, що підвищує стабільність приладів. Крім того, використання структури MQW дозволило покращити колірні характеристики OLED, зробивши їх більш насиченими та точними, що важливо для комерційних застосувань, таких як дисплеї та системи освітлення.

Ключові слова: Органічний світлодіод, Квантові ями, Ефективність, Гетероструктура, Яскравість, Екситон.