Journal of the Korean Applied Science and Technology
Vol. 39, No. 5. October, 2022. 589~595
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2022.39.5.589

안트라센의 단순 유도체와 루브렌을 이용한 백색 유기전기발광소자

김시현[1]* · 이승희[2]†

[1]BCP 주식회사, 신물질개발팀
[2]홍익대학교 바이오화학공학과
(2022년 6월 15일 접수: 2022년 10월 24일 수정: 2022년 10월 24일 채택)

White Oganic Light-Emitting Diodes based on Simply Modified Anthracene and Rubrene

Si-Hyun Kim[1]* · Seung-Hee Lee†

[1]*BPC Co., Ltd.*
[2]*Department of Bio & Chemical Engineering, Hongik university*
(Received June 15, 2022; Revised October 24, 2022; Accepted October 24, 2022)

요 약 : 안트라센의 골격을 갖는 청색 발광 물질, 9-(2-naphthyl)-10-(p-tolyl)anthracene (2-NTA)를 기본으로 하고, 오렌지 도판트인 루브렌을 다양한 부피비로 사용하여 백색 유기발광소자를 제작하였다. 그 결과 C.I.E. 좌표가 (0.32, 0.39)인 백색 유기발광소자를 얻었다. 다양한 부피비의 소자 중 루브렌을 1.5% 이하로 증착된 소자가 3% 이상으로 증착된 소자 보다 전기발광 효율이 높았다. 더욱이 2-NTA를 포함하는 백색 유기발광소자는 같은 조전하에서 2-NTA 만의 청색 유기발광소자 보다 낮은 턴온 전압을 갖는다. 결론적으로 2-NTA는 적은 양의 오렌지 도판트만으로 순수한 백색 유기발광소자를 구현할 수 있다.

주제어 : 백색 유기발광소자, 청색 발광, 나프틸 그룹, 안트라센, 루브렌, 도판트

Abstract : The white OLED is fabricated with the anthracene-based blue emitting material, 9-(2-naphthyl)-10-(p-tolyl)anthracene (2-NTA) in various volume-ratios of orange dopant, rubrene, which results in pure white emission with C.I.E. coordinate of ~(0.32, 0.39). The devices with 〈1.5% rubrene show better EL properties (efficiency) than 〉3% devices. Furthermore the turn-on voltage of 2-NTA WOLED (3.7 V) is lower than that of 2-NTA blue OLED (5.4 V) at the same condition. Conclusively 2-NTA with rubrene less than 1.5% (v/v) could be utilized for the pure WOLED.

Keywords : White organic light-emitting diodes, blue emission, naphthyl group, anthracene, rubrene, dopant

†Corresponding author
(E-mail: shleee@hongik.ac.kr)

1. Introduction

The issue about energy-saving gets more global attention, resulting in a big step of electronic devices. The more efficient, the smaller, the thinner, and the lighter things are pusued.

The OLED (organic light emission display) has been replaced for the LCD in the aspects of the efficiency, the thin shape, and the fast response. While in the LCD the light from the back light is passing through the liquid-crystal polymer and color filter, in the OLED the diode is self-emitting when the power is on. Therefore the OLED doesn't need any back light with low power consumption, and it responds at the moment of on-power for the fast motion display.

The research purpose for the OLED is mostly to get a natural full-color display, to get an efficient lighting equipment (white OLED)[1], and to lower the production cost. Firstly The color sensibility on red, green, or blue is quite different with the lowest on blue and the blue emitting materials usually have short life-time due to the large excitaion energy gap. Finding the long life-time blue emitting material or device mechanism is one of the OLED projects.

Secondly developing the more efficient and convenient conventional light source as daily necessities is pending project in respect to the energy saving.

Thirdly OLED is produced by chemical vapor deposition similarly to the semiconductors, very costly. In order to reduce the production cost, the total device mechanism may be changed.

In this paper, efficient white OLED for the conventional light source has been researched. The white light can be presented by the proper color composition of red, green, and blue emission (WOLED) resulting in proper C.I.E. data of (~0.3, ~0.3) and loner life-time[2~5]. Therefore in order to make up a white OLED (WOLED), the blue emitter has to be doped more than the green and the red ones. However, while the more emitter on the device would represent the brighter device, the stacking of the emitter has to be limited because of the intermolecular interaction inducing quenching. [6~11]

Conclusively a better WOLED needs RGB emitters with the proper emitting wavelengths and the proper spacial structure with less intermolecular quenching, and the proper amount of doping materials.

In this study, WOLED was made of an orange color emitter (rubrene) and a blue emitting material, 2-NTA (9-(2-naphthyl)-10-(p-tolyl) anthracene) which was synthesized in our lab [12] and for the proper doping ratio of two emitting materials to get better C.I.E. date for WOLED.

2. Experimental details

2.1. Synthesis of 2-NTA and characterization

Suzuki cross coupling reaction has been applied as in reference[12].

9,10-Dibromoanthracene (2.98 mmol) and 2-naphthyl boronic acid (2.98 mmol) were mixed in THF. 2M K_2CO_3 aqueous solution (50 ml) and tetrakis(triphenylphosphine) palladium (0.1 mmol) were added to the mixture. The resultant solution was refluxed for 8hr at 60℃. After cooling, the mixture was worked up, purified by column chromatography, and recrystallized in methanol to get white solid (92%).

All the chemicals are obtained from Sigma Aldrch Korea. ^1H- and ^{13}C-nmr spectra by JNM-Lambda Zeol Co., mass spectra by 5973N Mass selective detector, and elemental analysis by FLASH EA-2000 Thermo Scientific Co. have been obtained.

2.2. WOLED fabrication and measurement

The WOLEDs were fabricated in the following sequence: ITO(180 nm)/4,4-4,4',4''-tris[N-(1-naph thyl)-N-phenyl

amino]triphenylamine(2-TNATA)(30 nm)/4,4`-bis[N-(1-naphthyl)-N-phenyl-1-amino]biphenyl(NPB)(20 nm)/2-NTA(10 nm)/2-NTA: Rubrene (x %)(10 nm)/2-NTA(10 nm)/ TPBi(40 nm)/lithium quinolate(Liq)(2 nm)/Al (100 nm).

ITO coated glass with resistance of 10 Ω/sq was used as an anode for OLED. All the organic materials and the metal were deposited under the high vacuum. All the properties of the OLEDs such as current density (J), luminance (L), luminous efficiency (LE), and the C.I.E. chromaticity coordinates were measured with Roper Scientific Pro 300i, Keithley 2400, Chroma meter CS-1000A, and Roper Scientific Pro 300i.

3. Results and discussion

3.1. Results and discussion

Several bispiro-anthracene blue emitting materials have been used for the OLED fabrication in our lab [13]. Among the tested at the same condition, 1-NTA showed the luminous efficiency, the power efficiency, and the external quantum efficiency better than the other (1-NTA, 1-NFTA, 2-NFTA) [13].

Fig. 1 shows molecular structures of the organic materials used in this work. 2-TNATA and NPB are used as the hole-injection layer (HIL) and the hole-transporting layer (HTL), respectively. A blue emitting material 2-NTA, and a orange emitting material rubrene, are used for the white emitting layer. TPBi and Liq/Al are used as the electron-transporting layer and the composite cathode, respectively. Fig. 2 shows WOLED device structure in which the volume ratio of rubrene is changed from 0.5% to 7%.

As shown in Fig. 3 (a), 2-NTA emission band at 450 nm [12] is partially overlapped with the absorption band of rubrene at 500~530 nm and thus the energy can be transferred from 2-NTA to rubrene.

In Fig. 3 (a), decreasing the ratio of rubrene (increasing that of 2-NTA) makes the increasing the intensity of blue emission band at 450 nm and that of orange emission at 550 nm, implying that the more 2-NTA emits

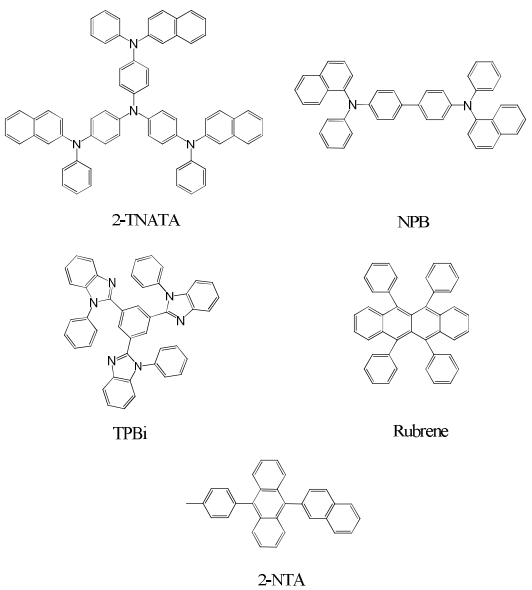

Fig. 1. The composite materials in this research.

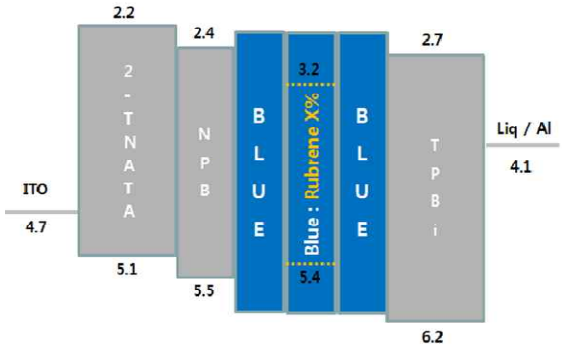

Fig. 2. WOLED structure with energy level (eV).

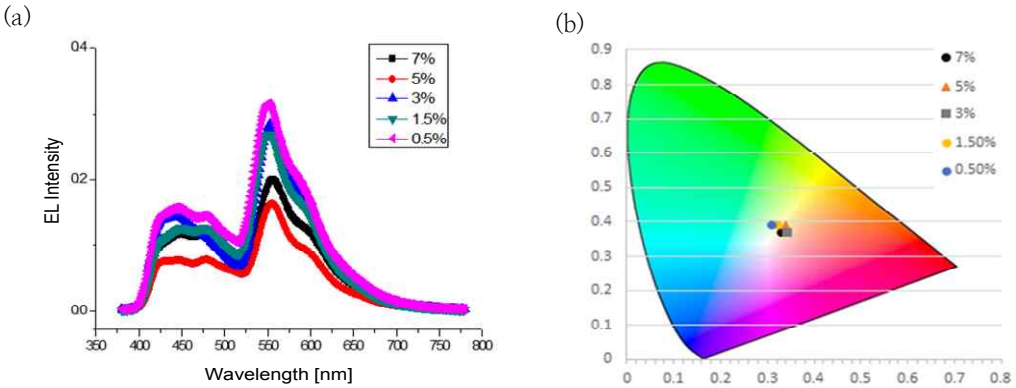

Fig. 3. (a) EL spectra and (b) C.I.E. coordinate of 2-NTA EL devices with various ratio of rubrene.

the more energy would transfer to rubrene.

In order to compensate the energy transfer from 2-NTA to rubrene and get white color, two additional blue emitting layers are added both above and beneath the emitting layer as shown in Fig. 2. The resulting C.I.E. coordinates are quite pure white of (0.31~0.34, 0.37~0.39) as shown in Fig. 3 (b).

The various volume ratios of rubrene to 2-NTA have been applied from 0.5% to 7% and the EL properties are explored (Table 1). The C.I.E coordinates, turn-on voltages at 1.0 cd/m², and luminance are similar to each other, not relevant with the ratio of rubrene.

Fig. 4 indicates that the EL data can be divided into two groups, less than 1.5% rubrene and more than 3%. The devices with less than 1.5% rubrene show better EL properties, luminous efficiency and external quantum efficiency.

The EL properties were compared with those of WOLED [14] as shown in Table 1. The reference data was about the device with a single layer (30 nm) of ADN rather than 3 layers of 2-NTA (10 nm x 3).

The device with 0.5% rubrene can be compared: low turn-on voltage (3.7 V vs. 4.8 V) at 1 cd/m^2 and maximum luminous (5.83 cd/A vs. 3.7 cd/A) and power efficiency (3.58 lm/W vs. 1.72 lm/W).

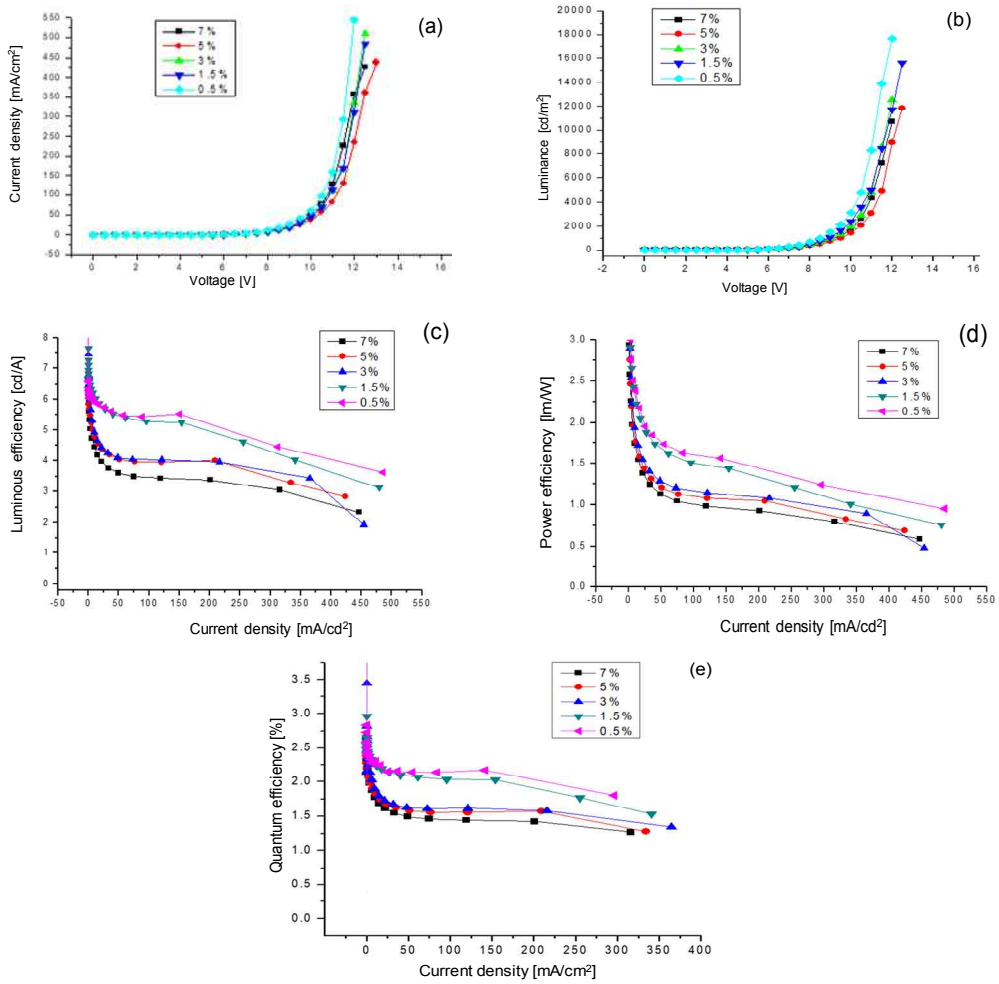

Fig. 4. The EL properties of WOLED with various rubrene composition: (a) L-V characteristics, (b) J-V characteristics, (c) luminous efficiency, (d) power efficiency (e) quantum efficiencies.

Table 1. EL properties of WOLED devices

Volume ratio of rubrene	7%	5%	3%	1.5%	0.5%	Reference*
λ_{max}, nm	422/556	420/556	427/553	423/550	420/550	455/545
C.I.E	0.33, 0.37	0.34, 0.39	0.33, 0.37	0.32, 0.39	0.31, 0.39	0.33, 0.43
V_{on}, V	3.7	3.8	3.8	3.8	3.7	4.8
L_{max} cd/m^2	10680	11780	12540	15620	17620	11700
LE, cd/A	4.00	5.30	4.50	5.75	5.83	3.7
PE, lm/A	1.98	3.05	3.24	2.90	3.58	1.72
EQE, [%]	2.44	2.48	2.81	2.96	2.83	-

*OLED with a single layer of the blue emitting ADN [13]

4. Conclusion

White light can be obtained by combination of red and blue emission layer in OLED. For the effective WOLED, the blue emitting materials with low sensibility have to be selected and doped in a proper amount.

In the previous report, two-emitter WOLED (NPB/rubrene 2%/ADN/Alq3) [15] was fabricated without blocking layer resulting in C.I.E. coordinates of (0.344, 0.372) and 30mA/cm2 [15], and WOLED with double white emissive layer (MADN/blue BCzVBi, MADN/red DCJTB) was reported to give C.I.E. coordinates of (0.36, 0.34) and quantum efficiency of 4.23% [16].

The C.I.E. data (0.31, 0.39) of 2-NTA:rubrene (0.5%) implies 2-NTA with rubrene could be utilized for the white OLED. The C.I.E. coordinates can be compared with (0.33, 0.43) of ADN:rubrene (0.5%). The difference could be originated from 2 factors: (1) utilizing the ETL material, TPBi, rather than Alq3 which emits green color, and (2) fabricating 3 emission layers of 2-NTA (10 nm)/2-NTA :rubrene (10 nm)/2-NTA (10 nm), which makes up for the low color sensitivity of the blue.

Turn-on voltages (V_{on}) are indepen- dent of the dopant concentration: V_{on} of 3.7~3.8 V with 1.0 cd/m^2, 30 nm. It is lower than that of the blue-only OLED with 2-NTA (5.4 V) at the same condition [11]. The energy levels of dopant, rubrene, would be the steps for the electron from the cathode, resulting in low V_{on}.

WOLED with rubrene less than 1.5% result in luminous, power, and quantum efficiencies better than those with more than 3%. The facts indicate that rubrene can help the EL property of 2-NTA. However, more than 3% of rubrene could interfere the blue emission mechanism.

In conclusion, 2-NTA can be utilized for the white OLED with rubrene as a dopant and the ratio of rubrene should be used less than 1.5% in this case.

Acknowledgement

This work was supported by Hongik University.

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