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Electroluminescence Properties of Simple Anthracene Derivatives Containing Phenyl or Naphthyl Group at 9,10-position for the Blue OLED

Si Hyun Kim · Song Eun Lee · Kim Yong Kwan · Seung Hee Lee†

Department of Chemical System Engineering, Hongik University, Sejong 2639, Korea
Department of Information Display, Hongik University, Seoul, 121-791, South Korea
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Abstract : The organic light-emitting diodes are fabricated with six anthracene derivatives containing simple substituents such as phenyl or naphthyl group. The device structure is as in the following: Indium tin oxide (ITO) (180 nm)/4,4-4,4`,4``-tris[N-(1-naphthyl)-N-phenylamino]triphenylamine (2-TNATA) (30 nm)/4,4`-bis[N-(1-naphthyl)-N-phenyl-1-amino] biphenyl (NPB) (20 nm)/Emitting compound (30 nm)/2,2′,2"- (1,3,5-Benzinetriyl)-tris (1-phenyl-1-H-benz-imidazole) TPBi (40 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm). In the emitting layer the anthracene derivatives are used without any dopant. All the six devices show blue emissions. Among the tested diodes, the one with 9-(2-naphthyl)-10-(p-tolyl) anthracene (2-NTA) exhibited luminous efficiency, power and external quantum efficiencies of 3.26 cd/A, 0.98 lm/A, 2.8 % at 20 mA/cm^2.

Keywords : Blue OLED, anthracene, Naphthyl group, Blue emission

1. Introduction

In order to get a natural color display, three color factors of red, green, and blue have to be presented with the similar efficiency[1,2]. The red and green color emitting materials so far show the long lifetime and emitting efficiency high enough to be used for the displays[3-5]. The blue color emitting materials, however, show much shorter lifetime than the others due to the intrinsic energy gap of the compounds[6-8].

Therefore photochemically stable and efficient blue materials are the pending project. Among the blue emitters, the anthracene derivatives are regarded as the proper blue emitters in organic light-emitting diode (OLED), which present promising phto luminescence (PL) and elctro luminescence (EL) properties and easy processability as well as good thermal stability[9-14].

During the cell fabrication by vacuum deposition, molecular aggregation could cause the self-quenching resulting in EL efficiency reduction. The derivatization of anthracene at 9,10-position could restrict the exciplex production.

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

In this work, the anthracene derivatives substituted at 9,10-position with some simple aryl group such as tolyl or naphthyl group were used for the blue OLED EL study.

2. Experimental details

2.1. Synthesis and characterization

The blue emitting materials were synthesized using Suzuki cross coupling reaction as in the reference[17], under N2 condition. 1H- and 13C-NMR were measured on JNM-Lambda series Zeol Co in CDCl3. Low resolution mass spectroscopy were measured by 5973N Mass selective detector. Elemental analysis was carried out on a FLASH EA-2000 Thermo Scientific Co.

2.2. Physical measurement

Absorption and Florescence spectra were measured in cyclohexane using Evolution 60 s and Cary Eclipse, respectively. Thermogravimetric analysis was conducted using N-1000 system at a heating rate of 10 ℃/min from 25 to 500 ℃.

2.3. OLED fabrication and measurement

ITO thin film coated on glass substrate with sheet thickness of 1500 Å and resistivity of 10 Ω/sq was used and washed with acetone, methanol, deionized water, and ethyl acetate in sequence for 15 min. Before loading chamber, any shadow particles on the ITO glass are removed by vacuum. All the organic materials and the metal for the electrode were deposited under high vacuum (8 × 10-7 Torr) condition.

The OLEDs were fabricated as in Fig. 1: ITO (180 nm)/4,4-4,4`,4``-tris[N-(1-naphthyl)-N-phenylamino]triphenylamine (2-TNATA) (30 nm)/4,4`-bis[N-(1-naphthyl)-N-phenyl-1-amino]biphenyl (NPB) (20 nm)/anthracene derivative (30 nm)/2,2′,2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benz-imidazole) (TPBi) (40 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm).

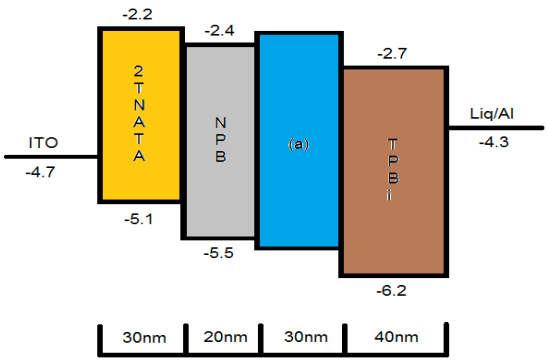
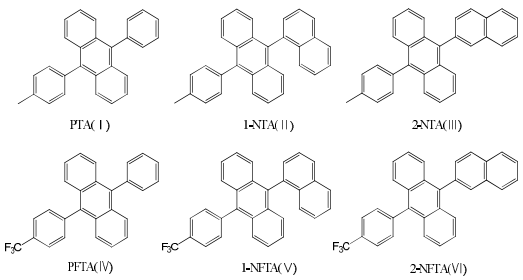


Fig 1. Energy level diagram of the materials used in OLED I-VI.

2-TNATA was used as the HIL, NPB as the HTL, TPBi as the ETL, and Liq/Al as the composite cathode. As the blue emitting layer, the previously reported anthracene derivatives (in Scheme 1, [17]) were used. All of the properties of the OLEDs such as current density (J), luminance (L), luminous efficiency (LE), and the CIE chromaticity coordinates were measured using Keithley 2400, Chroma meter CS-1000A. All measurements were carried out at room temperature under ambient conditions.



Scheme 1. Blue emitting compounds.

3. Results and discussion

Fig. 2 and 3 show the UV-vis absorption and PL spectra, respectively. Absorption bands of PTA (355/375/395 nm) were sifted

bathochromically from that of anthracene (340/356/379 nm) as shown in Fig. 2. PL bands of PTA (416/430/444 nm, as in Fig. 3) were also red-shifted from that of anthracene (400 nm). This band shift to low energy implies some π-conjugation between anthracene and phenyl or naphthyl groups.

The compound were thermally stable upto 300℃, enduring the vacuum deposition for the OLED. EL spectra in Fig. 4 show that maximum emitting bands range from 420 to 430 nm of blue color emission.

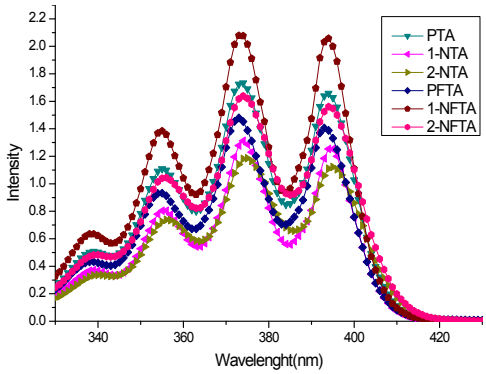


Fig 2. Absorption spectra of compounds in cyclohexane.

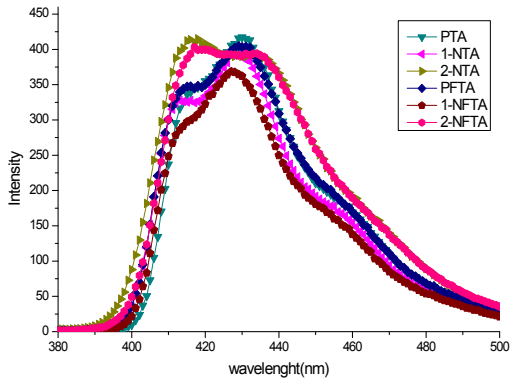


Fig 3. Emission spectra of compounds in cyclohexane.

Luminance-voltage, power efficiencies (PE), and external quantum efficiencies (EQE) of the devices I~VI are shown in Fig. 5 and the data are summarized in Table 1.

Band gaps between highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital (LUMO) are similar each other (3.2~3.05 eV). Turn-on voltage of device Ⅰ~Ⅵ are 6.5, 5.4, 5.1, 5.7, 9.7, and 9.6 V respectively. LE at current density of 20 mA/cm2 are 0.5, 2.04, 3.26, 3.04, 2.44, and 2.87 cd/A. PE at the same condition are 0.11, 0.58, 0.98, 0.85, 0.52, and 0.61 lm/A. EQE are 0.33, 1.78, 2.8, 1.94, 1.65, and 1.93 %.

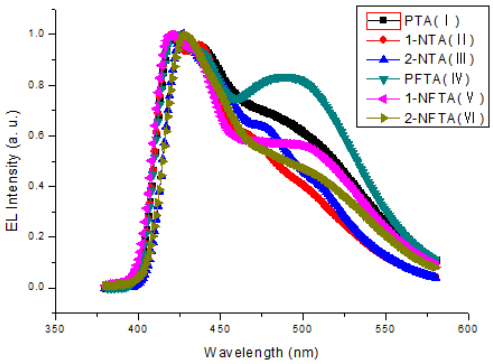


Fig 4. El spectra of devices Ⅰ~Ⅵ.

In result, turn-on voltages of devices are Ⅲ〈Ⅱ〈Ⅳ〈Ⅰ〈Ⅵ~Ⅴ and EL efficiencies are Ⅲ〉Ⅳ~Ⅵ〉Ⅱ〉Ⅴ〉Ⅰ. Device III has the highest LE with the lowest turn-on voltage. Devices IV has quite high LE with reasonable turn-on voltage.

Commission Internationale de l'Eclairage (CIE) data indicate all the devices are blue-emitting and the device III shows more deep-blue color compared with the device IV.

The EL properties of the device III including 2-NTA were comparable to that of the one with the bispiro-type anthracene derivatives with fluorene[15], as shown in Table 1. The latter exhibited LE of 1.71 cd/A, PE of 1.34 lm/A, EQE of 1.67 % at 20 mA/cm^2, and turn-on voltage of 2.7 V, while the former showed 3.26 lm/A, 2.8 %, and 5.1 V, respectively. Even though the device Ⅲ has higher turn-on voltage of 5.1 V than the bispiro-type one (2.7 V), it shows better LE and EQE.

Table 1. EL properties of the devices in this work compared the one with bispiro-anthracene

Devices	λ_{max} [nm]$^{(a)}$	C.I.E$^{(b)}$	E_g [eV]$^{(c)}$	V_{on} [V]$^{(d)}$	L [cd/m^2] $^{(e)}$	LE [cd/A] $^{(e),(f)}$	PE [lm/A]$^{(e),(f)}$	EQE [%]$^{(e)}$
Ⅰ(PTA)	422	(0.173, 0.169)	3.04	6.5	1081	0.56/0.5	1.29/0.11	0.33
Ⅱ(1-NTA)	420	(0.162, 0.146)	3.05	5.4	2439	2.05/2.04	0.99/0.58	1.78
Ⅲ(2-NTA)	427	(0.158, 0.144)	3.02	5.1	4547	3.35/3.26	1.52/0.98	2.8
Ⅳ(PFTA)	423	(0.167, 0.230)	3.04	5.7	2784	3.08/3.04	1.19/0.85	1.94
Ⅴ(1-NFTA)	420	(0.173, 0.204)	3.04	9.7	2301	2.55/2.44	1.74/0.52	1.65
Ⅵ(2-NFTA)	429	(0.172, 0.185)	3.02	9.6	2347	2.88/2.87	1.84/0.61	1.93
bispiro-type anthracene[16]	447	(0.150, 0.120)	3.02	2.7	1759	1.84/1.71	1.68/1.34	1.67

(a) EL spectra; (b) CIE coordinates (x,y); (c) Energy level measured by absorption edge[16]; (d) At 1.0 cd/m^2; (e) Maximum efficiency; (f) Efficiency at current density of 20 mA/cm^2

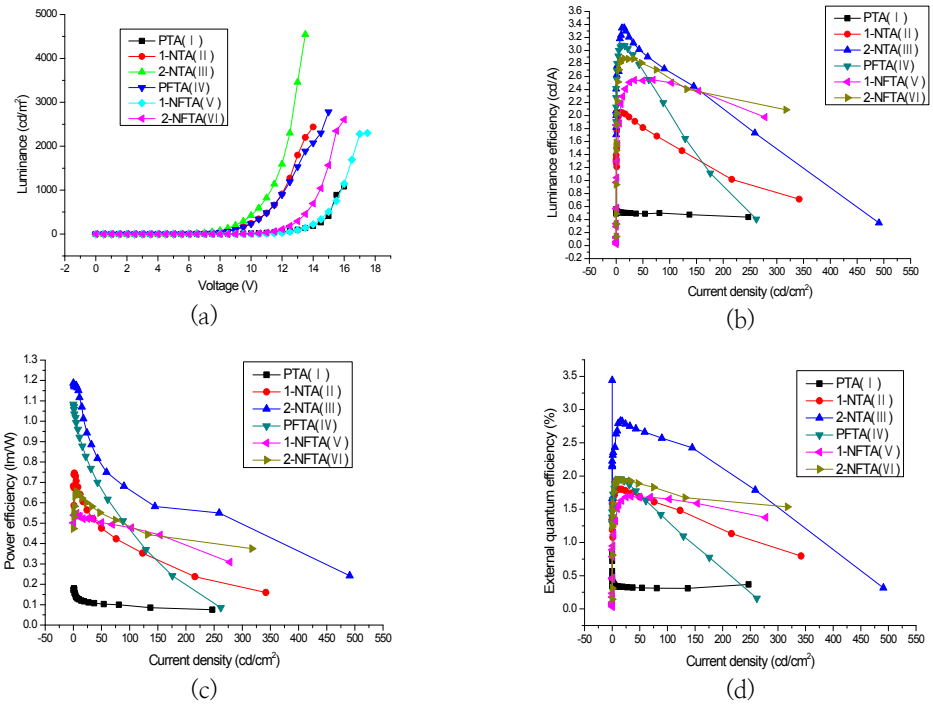


Fig 5. (a) Luminance-voltage, (b) Luminous efficiency (LE), (c) Power efficiency (PE), and (d) External quantum efficiency (EQE) of the device Ⅰ~Ⅵ.

4. Conclusion

The OLED containing the anthracene derivatives with simple substituents such as phenyl or naphthyl groups are fabricated and characterized. All the diodes in this work are emitting deep blue color. Among them, device Ⅲ using 2-NTA exhibited a LE of 3.26 cd/A, PE of 0.98 lm/A, EQE of 2.8 % at 20 mA/cm^2, and CIE coordinates of (0.158, 0.144), which indicate a good candidate for the blue OLED. The 2-NTA has a non planar molecular shape (dihedral angle 94° between anthracene and naphthyl palne) and thus vapour deposition doesn't make exciplex as much as non-derivatized anthracene, which could guarantee the stability and thus the efficiency in the diode.

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