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New Blue-Light Emitting Materials in White OLED Based on Solution and Vacuum Methods

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New host material of 2-tert-butyl-9,10-bis(3'',5''-diphenylbiphenyl-4'-yl)anthracene [T-TAT] substituted t-butyl group was investigated in solution process WOLED device compared with 9,10-bis(3'',5''-diphenylbiphenyl-4'-yl)anthracene [TAT]. A two-color WOLED of a co-host system using solution process method was demonstrated. The device configuration was ITO / PEDOT:PSS (40 nm) / emitting layer (50 nm) / TPBi (20 nm) / LiF (1 nm) / Al. The emitting layer consisted of TAT or T-TAT, NPB, DPAVB (blue dopant), and rubrene (yellow dopant). NPB was used to help hole carrier transport as well as blue host role. The device using the T-TAT compound as a co-host showed a luminance efficiency of 2.73 cd/A, which is 77% higher than TAT device of 1.54 cd/A at 20 mA/cm².

Keywords Organic light-emitting diode; host material; solution process; white OLED

Introduction

Many researchers have extensively studied to make high performance organic light-emitting diode (OLED) devices. [1–4] Especially, The interest based on white OLED (WOLED) has been rapidly growing in large full color display such as OLED TV and lighting fields. [5] Until now, WOLED has been produced using vacuum evaporation method, but this method involves disadvantages such as high cost, difficulties of large scaling and adjusting doping concentration. [6, 7] Therefore, there are many researches on methods of producing solution processed WOLED such as spin-coating, nozzle printing, and ink-jet printing method for their advantages of large scaling and relatively inexpensive cost. [8, 9]

A lot of approach ways for WOLED have been reported since the first report of Kido group. [10] Many researchers are also involved in ongoing efforts to make two or three emissive layers in OLED device. Also, because host-dopant system can significantly improve efficiency and show stable color purity, it was often used in WOLED. Especially, in order to develop the host for high performance, many molecules were designed and synthesized. A system that shows high efficiency with a hole or electron transporting material blended with emitting compounds is being actively considered as a co-host system. [11]

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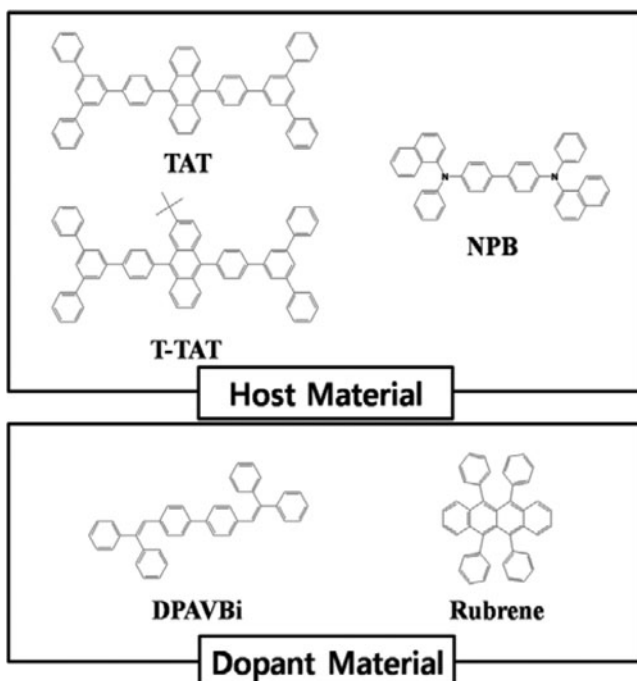


Figure 1. Chemical structures of materials.

In this study, two color white EML is proposed by using blending and spin-coating method through a co-host/dopant system. Device performances were systematically compared based on TAT or T-TAT and NPB as co-host.

Experimental

The method of synthesis for TAT in figure 1 is published in J. Mater. Chem.. [12] The synthesized method of T-TAT was published in other journal. [13]

9,10-Bis(3'',5''-diphenylbiphenyl-4'-yl)anthracene [TAT], 2-tert-butyl-9,10-bis(3'',5''-diphenylbiphenyl-4'-yl)anthracene [T-TAT] and N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) were used for the host substances used in the emitting layer, and 4,4'-bis[4-(di-p-tolylamino)styryl]biphenyl (DPAVB) and (5,6,11,12)-tetraphenylnaphthacene (rubrene) were used as each blue and yellow as the dopant substances. TAT:NPB or T-TAT:NPB was mixed in a mass ratio of 60:40 for host substances and DPAVB with ratio of 4% and rubrene with ratio of 0.2% were mixed for dopant substances based on the mass of co-host. Solvent was toluene. A water-dispersed PEDOT/PSS mixture (Baytron P VP CH8000, H. C. Starck GmbH) was spin-coated on top of indium tin oxide (ITO) in air for 40 nm thickness. The spin-coated films were baked on a hot plate at 110°C for 5 minutes in air and 200°C for 5 minutes in N₂ glove box. The emitting layer was spin-coated to obtain a thickness of 50 nm. The solution-processed films of emitter were baked on a hot plate (110°C, 30 min) in N₂ glove box. Electron-transporting layers 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBi) with a thickness of 20nm were deposited by vacuum evaporation (at a pressure about 10⁻⁶ Torr). LiF (1 nm) and Al films were sequentially deposited on the electron-transporting

Table 1. Optical and electrical properties of TAT and T-TAT

Compounds	Solution ^a		Film ^b		HO	LU	Band
	UV _{max} (nm)	PL _{max} (nm)	UV _{max} (nm)	PL _{max} (nm)	MO (eV)	MO (eV)	Gap (eV)
TAT	374, 394	436	383, 403	451	-5.62	-2.68	2.94
T-TAT	376, 395	439	383, 402	452	-5.62	-2.71	2.91

^aChloroform solution (1×10^{-5} M), ^bFilm on glass

layer under vacuum (at a pressure about 10^{-6} torr). I–V–L characteristics of the OLED devices and EL spectra were obtained using a Keithley 2400 source measure unit and a Minolta CS-1000A spectrophotometer. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo spectroscopy (PL).

Results and Discussion

PEDOT:PSS and the emitting layer were made using spin-coating method, and the ETL layer and LiF/Al electrode were fabricated by thermal deposition method. Figure 1 shows the chemical structures of host and dopant materials. TAT and T-TAT are blue emitters as host materials. NPB is used as a co-host material which has HTL property and wide band gap similar to a blue emitter. DPAVB_i and rubrene were each used as blue dopant and yellow dopant.

The optical and electrical properties of TAT and T-TAT are summarized in Table 1. Figure 2 shows UV-Visible (UV-Vis.) absorption and PL spectra of the two compounds in chloroform solution and spin-coated film. UV-Vis. absorption in solution and film states of the two compounds shows the typical anthracene absorption band in the range of 350~403nm. PL maximum wavelengths of TAT and T-TAT were also measured at 436 nm and 439 nm in solution state, and at 451 nm and 452 nm in film state, respectively. TAT

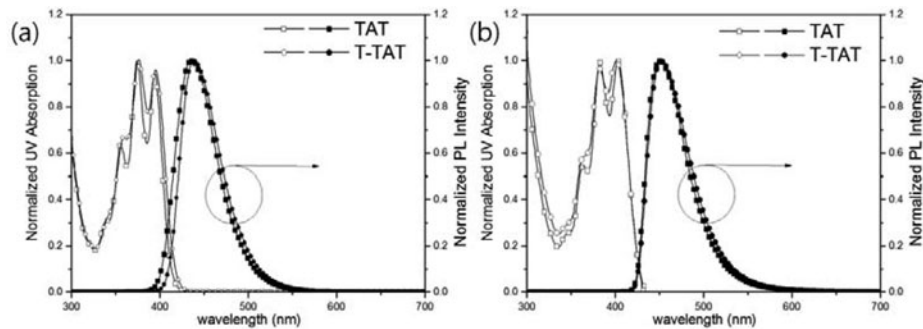


Figure 2. UV-Visible absorption and PL spectra of TAT (square) and T-TAT (circle): (a) solution in chloroform (1.0×10^{-5}), (b) spin-coated film.

Table 2. EL performances of WOLED devices: ITO/PEDOT (40 nm)/Emitting layer (50 nm)/TPBi (20 nm)/LiF (1nm)/Al (200 nm) at 20 mA/cm²

	L.E. ^a (Cd/A)	P. E. ^b (lm/W)	E.Q.E (%)	CIE(x,y)	EL _{max} (nm)
TAT	1.54	1.30	0.71	(0.30, 0.39)	467, 550
T-TAT	2.73	1.98	1.20	(0.28, 0.38)	469, 550

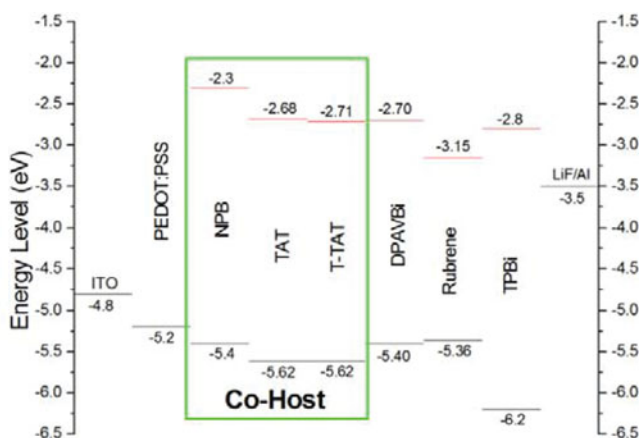
^aLuminance efficiency; ^bPower efficiency

and T-TAT with t-butyl group exhibited similar optical maximum values similar to UV-Vis. absorption and PL spectra.

Optical band gap was measured and calculated by UV-Vis. absorption spectrum of solid state. Band gap obtained from onset of absorption was 2.94 eV for TAT and 2.91 eV for T-TAT. The value of highest occupied molecular orbital (HOMO) level was obtained from AC-2, and the lowest unoccupied molecular orbital (LUMO) level was calculated by the use of HOMO level and optical band gap. The values of HOMO and LUMO level were measured to be −5.62 eV, −2.68 eV for TAT and −5.62 eV, −2.71 eV for T-TAT, respectively.

The device structure was fabricated as ITO/PEDOT (40 nm)/emitting layer: TAT or T-TAT + NPB + dopants (50 nm)/TPBi (20 nm)/LiF (1 nm)/Al. Device performances of WOLED using TAT or T-TAT are summarized in Table 2. Figure 3 shows energy diagrams of materials used in the WOLED device. Energy levels of TAT, T-TAT and NPB hosts were properly matched with those of dopants.

Solution processed WOLED devices were fabricated by spin-coating method using co-host of TAT or T-TAT and NPB as well as dopants. Figure 4 shows the luminance (cd/A) efficiencies versus current density of TAT and T-TAT. WOLED devices based on TAT or T-TAT showed luminance efficiencies of 1.54 cd/A and 2.73 cd/A at 20 mA/cm², respectively. Power efficiencies (lm/W) were 1.301 m/W and 1.981 m/W. T-TAT in which t-butyl group was added at 2-position of anthracene showed higher efficiency than TAT

**Figure 3.** Energy diagrams of materials in WOLED device.

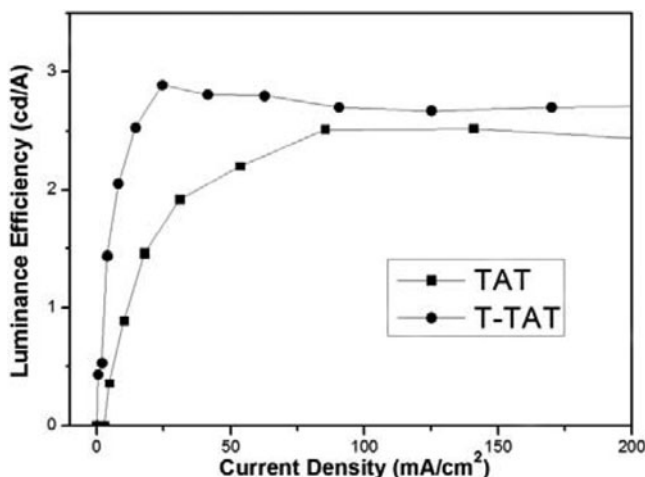


Figure 4. Luminance efficiency of EL devices: ITO/PEDOT (40 nm)/Emitting layer (50 nm)/TPBi (20 nm)/LiF (1 nm)/Al (200 nm).

because t-butyl group can help to prevent $\pi-\pi^*$ stacking interactions between adjacent molecules in spin-coated film. [14] External quantum efficiency (E.Q.E) value of T-TAT was 1.20%, which is higher than 0.71% of TAT at 20 mA/cm². As shown in Figure 5, the EL maximum values of TAT and T-TAT were exhibited at 467 nm or 469 nm of blue emission and 550 nm of orange emission, respectively. In case of the CIE values, similar color coordinates of TAT and T-TAT were shown at (0.30, 0.39) and (0.28, 0.38).

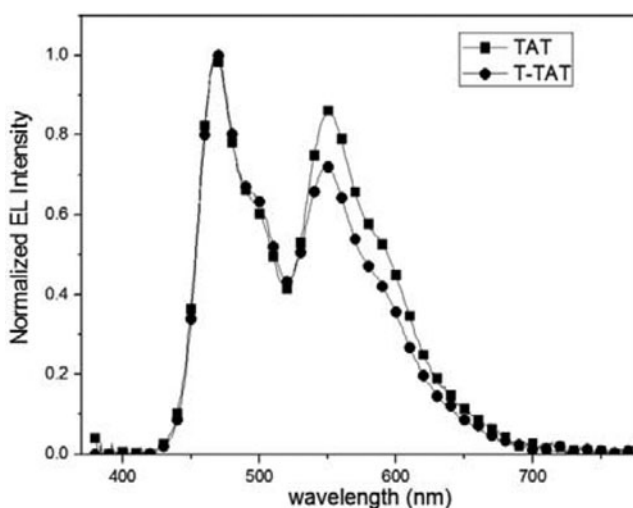


Figure 5. EL spectra of TAT (square) and T-TAT (circle).

Conclusions

WOLED devices were fabricated by spin-coating method based on co-host such as TAT or T-TAT with NPB. Also, DPAVB_i and rubrene were used as blue and orange dopants. Energy levels of host and dopant materials were properly matched. As a result, the device used T-TAT including t-butyl group as the co-host showed luminance efficiency of 2.73 cd/A, which is almost twice as high as 1.54 cd/A of TAT. Power efficiency also increased in T-TAT of 1.98 lm/W compared to TAT of 1.30 lm/W. CIE values of TAT and T-TAT device were respectively (0.30, 0.39) and (0.28, 0.38). In conclusion, WOLED device based on solution process including host material, a compound that includes substitution of t-butyl group into the anthracene core group showed higher performance than another compound device without t-butyl group.

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