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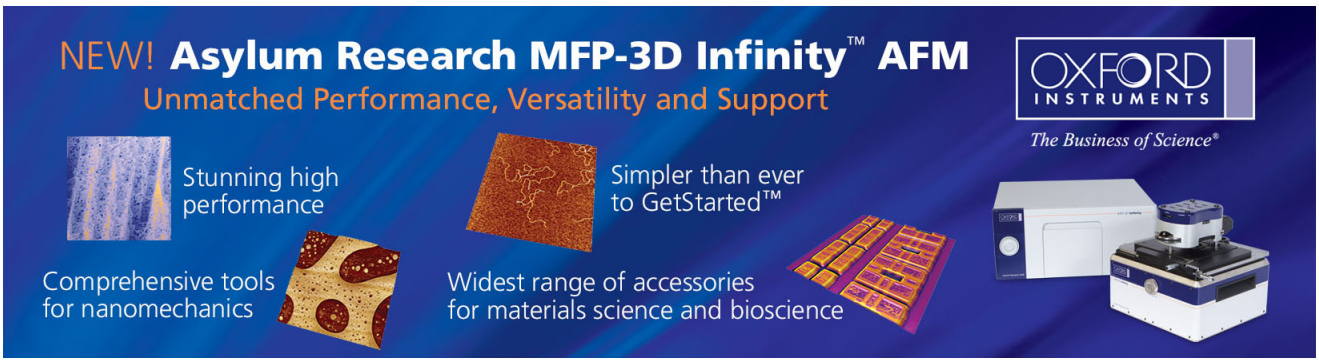

Highly efficient yellow and white organic electroluminescent devices doped with 2,8-*di*(*t*-butyl)-5,11-*di*[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthacene

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We describe the applications of a sterically-hindered yellow dopant, 2,8-*di*(*t*-butyl)-5,11-*di*[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthacene (TBRb) which, when compared to 5,6,11,12-tetraphenylnaphthacene (Rb) in either *tris*(8-hydroxyquinolinato)aluminum or 1,4-*bis*[*N*-(1-naphthyl)-*N*′-phenylamino]−4,4′ diamine (NPB) as host emitter, shows a 50%–34% increase in luminance efficiency over that of Rb device without significantly affecting its color. In addition, we have incorporated the TBRb doped yellow NPB emitter into the two-element white organic light-emitting diodes based on *p*-*bis*(*p*-*N*,*N*-*di*-phenyl-aminostyryl)benzene doped 2-methyl-9,10-*di*(2-naphthyl) anthracene sky-blue emitter which improved the luminance efficiency by 44% over that of Rb to 12.8 cd/A and 4.3 lm/W at 20 mA/cm^2 with CIE$_{x,y}$=[0.31,0.38]. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1803911]

5,6,11,12-Tetraphenylnaphthacene better known as rubrene (Rb), a highly fluorescent laser dye, has been primarily used as a yellow dopant in organic light-emitting diodes (OLEDs). Doped either in *n*-type host as in *tris*(8-hydroxyquinolinato) aluminum (Alq_3) or *p*-type host as in 1,4-*bis*[*N*-(1-naphthyl)-*N*'-phenylamino]biphenyl-4,4' diamine (NPB),[1] excellent yellow electroluminescence (EL) can be obtained due to its unique bipolar transport property.[2] Owing to the vividness and glittering effect of yellow electroluminescence similar to that of the inorganic ZnS:Mn emitter, pixels made from Rb are often combined with their complementary sky-blue color pixels and used in many of the small-sized area-color passive-matrix OLED panels on the market. However, generating a yellow EL is not the only application of Rb in OLEDs. In 1995, Hamada *et al.* obtained a highly efficient device by doping Rb in aromatic diamine[3] to make up a *p*-type yellow emitter. Based on this finding, Sato *et al.* has added another *n*-type sky-blue emitter in addition to Hamada's yellow device to fabricate a two-element white OLED.[4] In recent years, this white OLED architecture coupled with a red, green, blue (RGB) color filter has become increasingly popular as one of the major methodologies to fabricate full color devices.[5] This is primarily due to cost and mass production consideration in manufacturing as discreet RGB pixelation process can be accomplished without using the tedious and troublesome precision shadow mask.

In this letter, the luminance efficiency of the current two-element white OLEDs has been improved by modifying the dopant used in the yellow emitter. The primary objective was to modify the molecular structure of Rb in achieving better luminance efficiency without affecting its bipolar transport property and color. This is accomplished by introducing four bulky *tert*-butyl groups into the Rb molecule and thus, having synthesized 2,8-*di*(*t*-butyl)-5,11-*di*[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthacene, hitherto named as *tetra*(*t*-butyl) rubrene (TBRb). We doped TBRb into *n*-type and *p*-type emitting layers separately and our experimental results showed that TBRb, having greater steric hindrance, can effectively enhance the luminance efficiency of the device by over 50% and 34%, respectively. When the *p*-type emitter of TBRb is incorporated into the two-element white OLED composition based on *p*-*bis*(*p*-*N*,*N*-*di*-phenyl-aminostyryl) benzene (DSA-Ph) doped 2-methyl-9,10-*di*(2-naphthyl) anthracene (MADN) sky-blue emitter,[6] the total luminance efficiency can be improved by 44% without impacting on its white color Commission Internationale d'Eclairage (CIE) coordinates which are (0.31, 0.38).

Chemical structures of key materials that include TBRb, Rb, DSA-Ph and MADN studied in this report are depicted in Fig. 1. Rb was purchased commercially and purified by train sublimation and TBRb was synthesized in house.[7] By direct photoionization measurements (Riken AC-2), the lowest unoccupied molecular orbital/highest occupied molecular orbital level of TBRb is found to be at around 3.20/5.38 eV with a band gap energy (E_g) 2.18 eV that is essentially identical to that of Rb with 3.31/5.4 eV ($E_g \sim 2.18$ eV). Moreover, we adopted three device architectures in this study: Device **A** is a yellow device with Rb or TBRb doped in *n*-type material *tris*(8-hydroxyquinolinato)aluminum (Alq_3) as the yellow emitter; device **B** is a yellow device with Rb or TBRb doped in *p*-type material 1,4-*bis*[*N*-(1-naphthyl)-*N*′-phenylamino]biphenyl-4,4′ diamine (NPB) as the yellow

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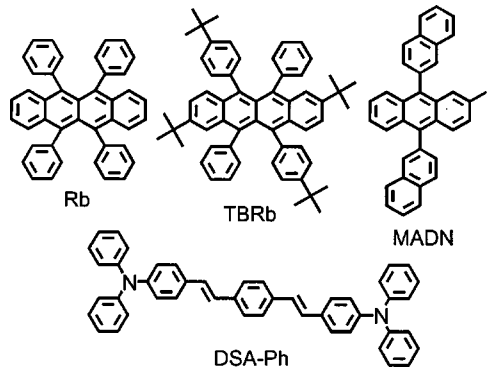

FIG. 1. Chemical structures of materials used in this study.

emitter; device **C** is a two-element white device in which a sky-blue emitter is combined with a yellow emitter (Rb or TBRb doped in NPB).

In device **A**, the structure was [indium tin oxide (ITO) (170 nm)/copper phthalocyanine (CuPc, 15 nm)/NPB (60nm)/wt% dopant: Alq_3 (37.5 nm)/LiF (1 nm)/Al (200 nm)], where ITO on glass (0.7 mm thick) has a sheet resistance of ~10 Ω/square, CuPc as the hole-injection layer, NPB as the hole transport layer, wt% dopant: Alq_3 as the emitter, Alq_3 as the electron transport layer and LiF/Al as the electron-injection layer and cathode. In device **B**, the Rb or TBRb was doped in NPB (20 nm) as a separate emitter where the hole-transport layer NPB was thinned to 40 nm while Alq_3 electron transport layer was increased to 75 nm to balance the injected carriers in the device. In device **C**, the yellow dopant concentration was fixed at 1.2%. MADN and DSA- Ph are the host and dopant of the sky-blue emitter, respectively. The thickness of each organic layer as well as dopant concentration has been adjusted to balance the injected carriers in the white device. The device structure is [ITO 170 nm/CuPc (15 nm)/NPB(50 nm)/1.2% Rb or TBRb: NPB (20 nm)/3% DSA-Ph: MADN (40 nm)/Alq_3 (15 nm)/LiF (1 nm)/Al (200 nm)]. Details of device fabrication have been described elsewhere.[7]

The plots of doping concentration (wt%) in Alq_3 versus luminance efficiency (cd/A) of TBRb and Rb at 20 mA/cm^2 are compared in Fig. 2(a). It is found that near saturated yellow color is reached only at over 5% doping where Rb has a $CIE_{x,y}=[0.50,0.49]$ and TBRb has a similar $CIE_{x,y}=[0.51,0.48]$. At 5% doping and a drive current density of 20 mA/cm^2 and voltage of 8.8 V, the EL efficiency of TBRb (5.6 cd/A and 2.0 lm/W) is more than 50% higher than that of Rb (3.7 cd/A and 1.3 lm/W). Detailed device attributes of TBRb and Rb doped (at 5%) emitters are compared in Table I.

In Fig. 2(b), we show the plots of doping concentration (wt%) in NPB versus luminance efficiency (cd/A) of TBRb and Rb at 20 mA/cm^2 drive condition in device **B**. Both dopants find their luminance efficiencies plateau after 2% and become essentially independent of the doping concentration. From 2% to 14%, TBRb has an efficiency of around 5.9 cd/A, which is more than 34% more efficient than that of Rb of 4.4 cd/A. At around 5% doping, Rb has a $CIE_{x,y}=[0.46,0.53]$ and TBRb has a similar $CIE_{x,y}=[0.47,0.51]$ that are quite different from those of device **A**. The EL spectra of 5% TBRb doped devices **B** has the emission max peak at 564 nm that is 8 nm hypsochromically shifted from that of

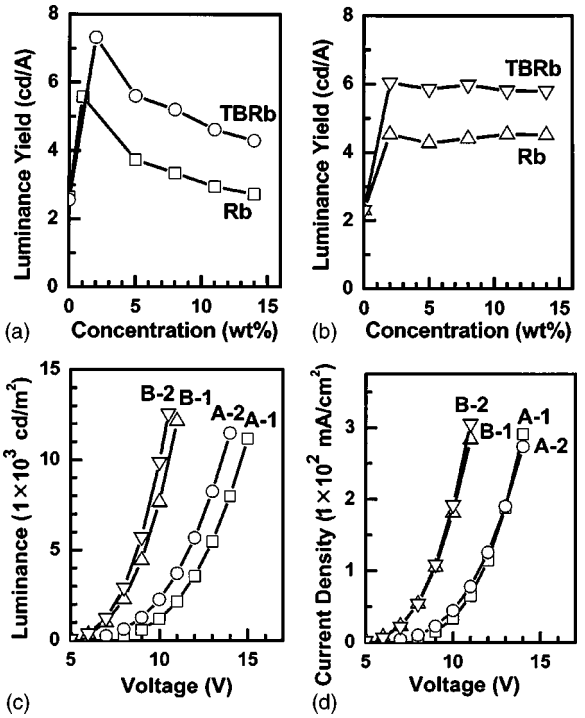

FIG. 2. EL characteristics of Rb and TBRb doped emitters: (a) luminance efficiency vs concentration of device **A** and (b) device **B**, (c) luminance vs voltage, and (d) current density vs voltage.

device **A** (λ_{max}~572 nm). From the profile of the EL spectrum of **B** (see Fig. 3), it is found that the emission of doped NPB device is composed of TBRb and a small amount of Alq_3 emission at λ_{max} 520 nm, which is apparently generated from carriers recombination in the Alq_3 near the interface of the emitter.[8]

Figure 4 is the EL spectra of Device **C**. Since human eyes are relatively less sensitive to blue light, it is therefore important to increase the blue portion in the white OLED. In order to increase hole/electron recombination in the blue emitter, we have purposely lowered the doping concentration of Rb and TBRb in NPB to 1.2%. In the device structure without yellow dopant in NPB (device **C-1**), a sky-blue color was observed with $CIE_{x,y}=[0.17,0.35]$ and the luminance efficiency of 7.5 cd/A at 20 mA/cm^2. Furthermore, the optimal doping concentration of DSA-Ph in achieving the highest brightness of blue in MADN is 3%. Detailed descriptions pertaining to the development of blue emitter including the synthesis and device structure tuning will be reported elsewhere.[9] To better observe the contribution of TBRb in

TABLE I. EL performance of 5% Rb and TBRb doped Alq_3 (**A**), NPB (**B**) emitters and white OLEDs (**C**) driven at 20 mA/cm^2.

Device	Yellow dopant conc. (%)	Voltage (V)	CIE *x*	CIE *y*	Lum. yield (cd/A)	Efficiency (lm/W)
A-1	Rb (5%)	9.3	0.50	0.49	3.7	1.3
-2	TBRb (5%)	8.8	0.51	0.48	5.6	2.0
B-1	Rb (5%)	6.9	0.46	0.53	4.3	2.0
-2	TBRb (5%)	6.9	0.47	0.51	5.9	2.6
C-1	none	9.4	0.17	0.35	7.5	2.5
-2	Rb (1.2%)	9.6	0.31	0.38	8.9	2.9
-3	TBRb (1.2%)	9.4	0.31	0.38	12.8	4.3

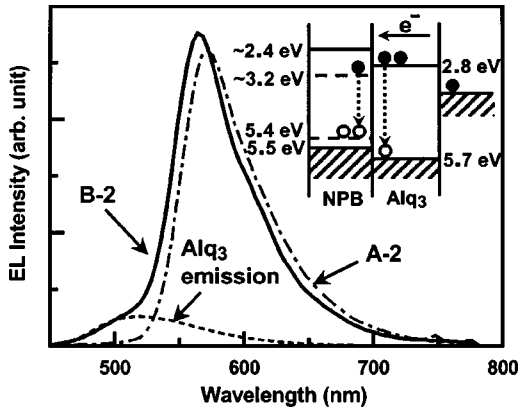

FIG. 3. EL spectra of 5% TBRb doped NPB and Alq_3 emitters at 20 mA/cm^2 inset is the energy level diagram of **B-2** device (in the vicinity of the emitting layer). The dashed line within NPB represents the energy level of TBRb, where (●) is an electron and (○) is a hole.

the white emission spectrum, the EL spectra in Fig. 4 have been normalized with the blue emission intensity. It is noted from the diagram that the yellow portion of the spectrum has significantly risen when TBRb was added as the yellow dopant in the white device. The device luminance efficiency has improved 44% from the original 8.9 cd/A to 12.8 cd/A without signiflcantly altering the blue emitter composition. This indicates that the results of the previous *p*-type yellow devices are applicable to the white device as well. The emission colors of the two white devices are similar with $CIE_{x,y}=[0.31,0.38]$.

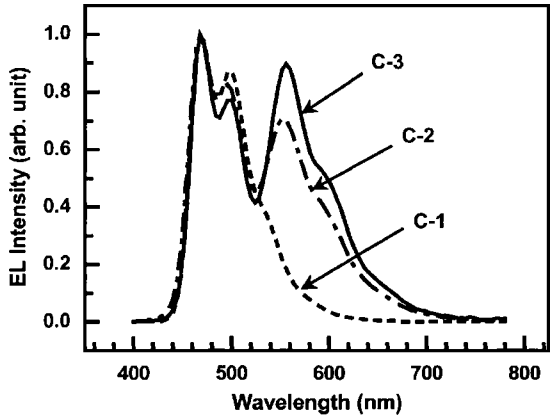

FIG. 4. EL spectra of device **C-1**, **C-2**, and **C-3** at 20 mA/cm^2.

In conclusion, we have synthesized a yellow dopant TBRb by introducing four *tert*-butyl groups into the molecular structure of Rb. The introduction of the passive bulky groups is found to alleviate the concentration-quenching problem by preventing inter-molecular aggregation of dopant molecules. The experimental results have indicated that highly efficient yellow OLED device can be obtained by doping TBRb into either *n*-type or *p*-type emitter. In comparison with the devices doped with Rb, the luminance efficiency at 20 mA/cm^2 has improved by 50% and 34% to reach 5.6 cd/A ($CIE_{x,y}=[0.51,0.48]$) and 5.9 cd/A ($CIE_{x,y}=[0.47,0.51]$), respectively. In addition, we have incorporated the TBRb doped yellow NPB emitter into the two-element while OLED based on DSA-Ph doped MADN sky-blue emitter which improved the luminance efficiency by 44% over that of Rb to 12.8 cd/A at 20 mA/cm^2 with $CIE_{x,y}=[0.31,0.38]$. The highly efficient white OLED should prove beneficial to the development of maskless fabrication process of full-color OLED displays if combined with the color filter technology.

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