



# Tunable red emission by incorporation of a rubrene derivative in *p*-type and *n*-type hosts in organic light emitting devices

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## ARTICLE INFO

### Article history:

Received 23 September 2008

Received in revised form 7 March 2009

Accepted 12 March 2009

Available online 24 March 2009

### Keywords:

Red-emitting

Rubrene-derivative

## ABSTRACT

A red-emitting rubrene derivative, 2-formyl-5,6,11,12-tetraphenyl-naphthacene (2FRb) was separately doped into 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) as the emitting layer. The emission can be tuned from 580 nm to 607 nm in NPB host and 560 nm to 622 nm in Alq<sub>3</sub> host. The Alq<sub>3</sub>-hosted devices show better performances: more saturated pure red emission peaking at 622 nm with CIE<sub>xy</sub> = [x = 0.65, y = 0.35], a maximum luminance efficiency of 2.42 cd/A and a maximum luminance of 3100 cd/m<sup>2</sup> by doping 3.2 wt.% 2FRb in Alq<sub>3</sub> host. It indicates that the derivative of rubrene is a promising bipolar dopant for red light-emitting device.

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## 1. Introduction

Organic light emitting devices (OLEDs) have attracted much more attention for their potential applications in flat panel display and solid state lighting in recent years [1,2]. However, as one component of white emission, red-emitting materials, there are still some challenges. Pyran-containing energy-transfer-typed compounds, such as, 2-[2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]-propanedinitrile [3] or 2-[2-(1,1-dimethylethyl)-6-[2-(2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H-benzo[*ij*]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]-propanedinitrile, mostly used as red dopant in tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) host [4], have been widely studied and regarded as the most important red dopants for OLED applications. The performance of devices with such red emitters is still unsatisfied, such as, low efficiency caused by charge-induced fluorescence quenching [5] and concentration quenching. Also, hole-cations sometimes [6] form easily so as to lower the operation efficiency and stability of the device. Besides choosing other proper hosts or co-hosted system for red dopants, molecular modification of charge-trap-typed compounds, like rubrene, might be another method to improve the performances of the red emitters. rubrene is commonly used as a yellow dopant [7,8] for that it has some attractive properties, such as, its near unity photoluminescent (PL) quantum efficiency and its bipolar

character [9], and it also can be used as an assistant dopant to overcome concentration quenching and further to improve the efficiency and operation stability [10–13] of the devices.

In this paper, a rubrene derivative, 2-formyl-5,6,11,12-tetraphenyl-naphthacene (2FRb) was separately doped into 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), as the *p*-type host and tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>), as the *n*-type host as the emitting layer. The electroluminescence (EL) emission can be tuned from 580 nm to 607 nm when doped into NPB host and from 560 nm to 622 nm when incorporated into Alq<sub>3</sub> host by adjusting their doping concentration in the emitting layer. The emission peak does not shift with voltage at one fixed doping concentration. The red-emitting Alq<sub>3</sub>-hosted devices shows better performance, such as, a maximum luminance efficiency of 2.42 cd/A and a maximum luminance of 3100 cd/m<sup>2</sup>, more saturated pure red emission peaking at 622 nm with the corresponding Commission Internationale d'Eclairage (CIE) coordinates of (x = 0.65, y = 0.35).

## 2. Experimental details

The chemical structure of 2FRb was shown in Fig. 1 and the synthesis process was as following: 6,7-disubstituted-1,4-naphthoquinone and 1,3-diphenylbenzofuran reacted in non-polar solvent under nitrogen protection, refluxed for several hours, the reaction process was traced by high pressure liquid chromatography and thin layer chromatography, the reaction intermediate was attained then reacted with phenyl lithium or phenyl magnesium bromide [14]. Other chemicals were commercially purchased without further purification.

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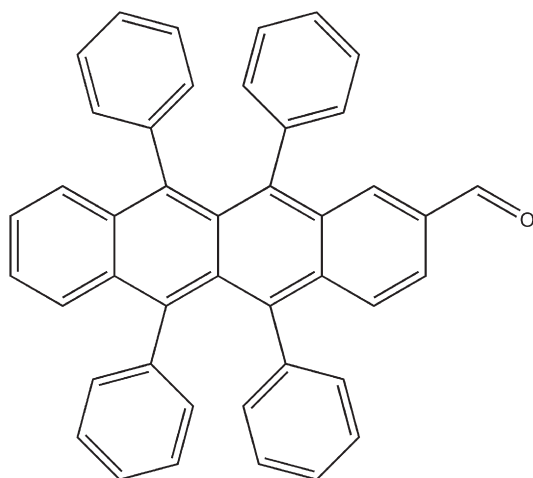


Fig. 1. The chemical structure of 2FRb.

Table 1

Electroluminescence performances of the 2FRb doped NPB devices.

Doping content (wt.%)	$\lambda_{\text{max}}$ (nm)	$\eta_{\text{c,max}}$ (cd/A)	Luminance (cd/m <sup>2</sup> )	CIE coordinates (x, y)
0.5	589	1.88	1600	(0.32, 0.23)
0.7	595	1.64	1292	(0.41, 0.29)
0.9	596	2.12	1283	(0.42, 0.33)
1.0	600	2.03	1267	(0.58, 0.40)
1.5	607	2.00	1285	(0.60, 0.40)

Two devices were fabricated with the structures as following,

Device 1: 2-TNATA (10 nm)/NPB (40 nm)/NPB:  $x$  wt.% 2FRb (10 nm)/TPBi (60 nm)/LiF (0.5 nm)/Al (200 nm) and  $x = 0.5, 0.7, 0.9, 1.0$  and  $1.5$  respectively.

Device 2: 2-TNATA (10 nm)/NPB (40 nm)/Alq<sub>3</sub>:  $y$  wt.% 2FRb (10 nm)/Alq<sub>3</sub> (50 nm)/LiF (0.5 nm)/Al (200 nm) and  $y = 0.2, 0.4, 0.6, 0.8, 1.6, 2.4$  and  $3.2$  respectively.

2-TNATA denotes 4,4',4''-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)tri-phenylamine for helping hole's injection and TPBi is 2,2',2''-(1,3,5-phenylene)tris(1-phenyl-1H-benzimidazole) functioning as electron transport and hole blocking.

### 3. Results and discussions

Fig. 2 shows the dependence of normalized spectra of 2FRb on doping concentration in NPB host in device 1 at the current density of 30 mA/cm<sup>2</sup>. We can note that there exist two emission peaks at 441 nm and around 590 nm originated from NPB and 2FRb, respectively. The emission peak of 2FRb red shifted with increasing doping content from 580 nm to 608 nm with the corresponding CIE coordinates changing from ( $x = 0.32, 0.23$ ) to ( $x = 0.60, 0.40$ ). At the doping concentration of 1.5 wt.%, there is no emission from NPB any more but a red emission from the dopant. The red emission gradually saturated with doping concentration. Table 1 summarized the EL performances of 2FRb doped NPB devices. Pure red emission with a luminance of 1285 cd/m<sup>2</sup>, an efficiency of 2.0 cd/A and CIE coordinates of (0.60, 0.40) was obtained at the doping content of 1.5 wt.% 2FRb in NPB hosted device.

The inset of Fig. 2 shows the schematic energy level diagram. Electrons injected into the 2FRb doped NPB can be easily captured by 2FRb, which has a much higher electron affinity than NPB. At low doping concentration, 2FRb molecules act as trap while as electron hopping pathway at high doping concentration. Moreover, holes injected into 2FRb doped NPB can be directly captured by 2FRb for the

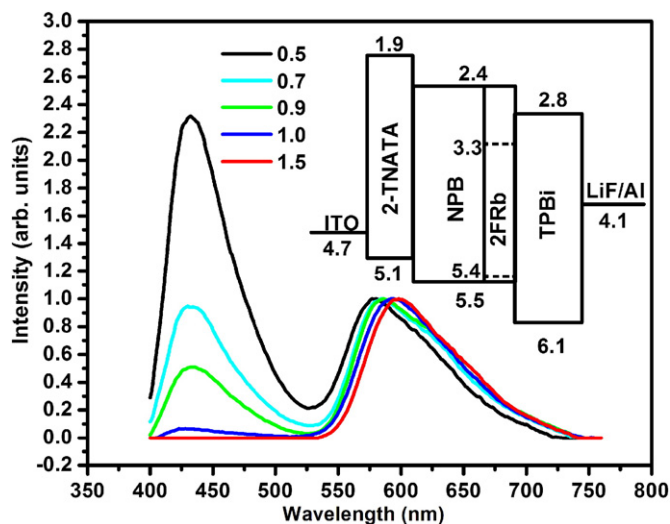


Fig. 2. The dependence of normalized spectra of 2FRb on doping concentration at the current density of 30 mA/cm<sup>2</sup> and the inset is the schematic energy level diagram.

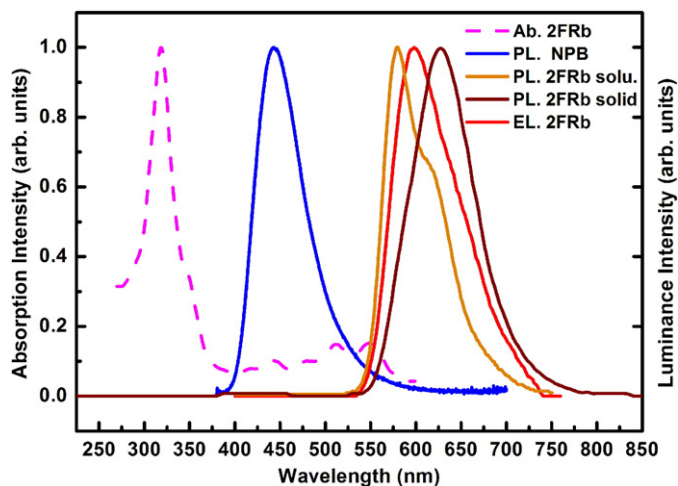


Fig. 3. The absorption and PL spectra of 2FRb in CH<sub>2</sub>Cl<sub>2</sub> solutions and PL spectra of neat NPB and 2FRb film and EL spectra of 1.5 wt.% 2FRb doped NPB device.

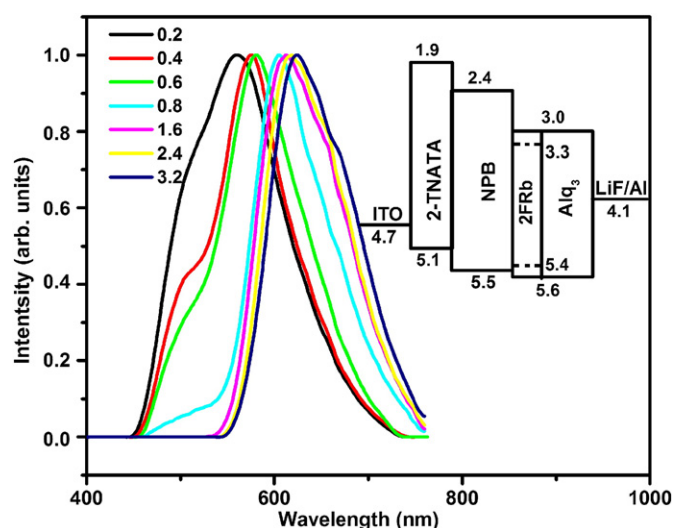


Fig. 4. The dependence of normalized EL spectra of 2FRb doped Alq<sub>3</sub> devices on doping concentration at the current density of 30 mA/cm<sup>2</sup> and the inset is the schematic energy level diagram.

shallow trap with 0.1 eV differences [8], so electron-hole recombination on the 2FRb molecules is predominant in 2FRb doped NPB device, and also the slightly spectral overlap of PL spectrum of NPB with absorption spectrum of 2FRb in Fig. 3 indicates that the process of energy transfer from the host to the dopant may occur, which plays minor role in the emission. The emission peak of PL spectrum of 2FRb in CH<sub>2</sub>Cl<sub>2</sub> solution is 580 nm, which is the same with that of EL spectrum of 0.5 wt.% 2FRb doped NPB, indicating the 2FRb molecules are dispersed individually and no intermolecular action with each other in host matrix. The emission peak of PL spectrum of neat 2FRb film is around 626 nm which might be caused by the strong interaction between the 2-formyl moieties introduced on the molecules. However, the efficiency of the device does not change with the doping concentration (see Table 1), that is, its efficiency and the luminance nearly keep the same at the doping content larger than 0.9 wt.%. It may be explained like this: the molecular modification of rubrene works, the emission spectra can be tuned by its doping concentration while it keeps some attractive properties from rubrene, that is, the luminance and the efficiency saturate at high doping content. This is neither like that of DCJTb doped Alq<sub>3</sub>, in which the spectra red shift and efficiency lower down with increasing doping levels<sup>3</sup>, nor rubrene doped NPB device, in which the spectra is not shifted with doping concentration while the luminance saturates at high doping levels [8].

Also, 2FRb was doped into Alq<sub>3</sub> host. We can find the devices have the same excitation mechanism in NPB hosted devices. Fig. 4 shows the dependence of normalized EL spectra of 2FRb doped Alq<sub>3</sub> devices on doping concentration at the current density of 30 mA/cm<sup>2</sup>. The doping content was ranging from 0.2 to 3.2 wt.% and the EL emission peak shifted from 560 nm to 622 nm with the CIE coordinate shift from (0.37, 0.51) to (0.65, 0.35). The luminance and efficiency saturated at high doping concentration. They showed larger red

Table 2  
Electroluminescence performances of the 2FRb doped Alq<sub>3</sub> devices.

Doping content (wt.%)	$\lambda_{\text{max}}$ (nm)	$\eta_{\text{c,max}}$ (cd/A)	Luminance (cd/m <sup>2</sup> )	CIE coordinates (x, y)
0.2	560	4.50	13,603	(0.37, 0.51)
0.4	572	3.02	10,275	(0.40, 0.50)
0.6	578	2.95	16,483	(0.46, 0.49)
0.8	605	2.80	6412	(0.59, 0.41)
1.6	613	2.76	5350	(0.60, 0.40)
2.4	617	2.70	4950	(0.62, 0.38)
3.2	622	2.42	3100	(0.65, 0.35)

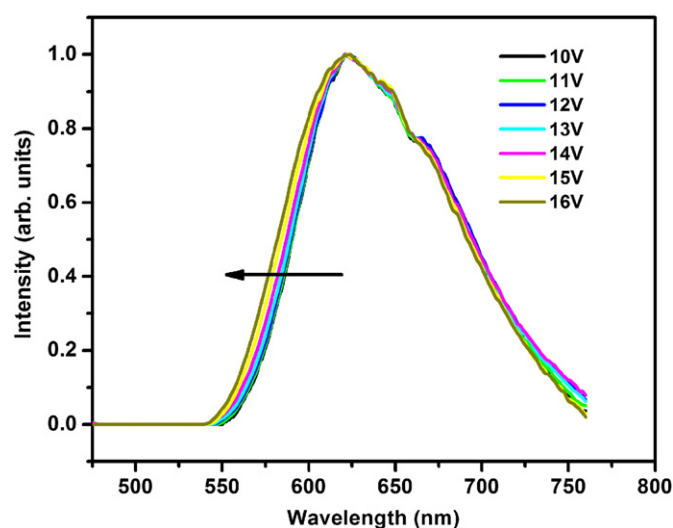


Fig. 5. The dependence of normalized EL spectra of 3.2 wt.% doped Alq<sub>3</sub> device on applied bias.

shift (see Table 2) than that of NPB hosted devices: at 3.2 wt.% 2FRb doped Alq<sub>3</sub> device, it has a maximum efficiency of 2.42 cd/A, a maximum luminance of 3100 cd/m<sup>2</sup> and a pure red emission peaking at 622 nm with CIE coordinates of (0.65, 0.35), respectively. This may attribute to that of the differences of intrinsic properties and polarity between the *p*-type host and *n*-type hosts [3]. Also, we can noticed that the efficiency was kept at 2.7 cd/A at high doping concentration while it lowers to 2.42 cd/A at 3.2 wt.% doped device, this might be caused by the de-trapping process at very high doping concentration, it can be supported by the slight blue-shift of the emission with the increasing voltage indicated in Fig. 5. Also, it is interesting to find that the emission peak is stable with voltage at one fixed doping concentration in Fig. 5, which is the same with rubrene doped device. Fig. 6 shows the PL and absorption spectra of 2FRb in CH<sub>2</sub>Cl<sub>2</sub> solutions and neat film and PL spectra of neat Alq<sub>3</sub> film and EL spectra of 3.2 wt.% 2FRb doped Alq<sub>3</sub> device. The larger spectral overlapping between the absorption spectrum of 2FRb and emission spectrum of Alq<sub>3</sub> film than that of NPB film indicates that energy transfer process in Alq<sub>3</sub> hosted device is favorable. The inset of Fig. 4 shows the schematic level diagram of the devices. The injected holes directly trapped on the molecules. Charge trapping is the main EL mechanism.

In summary, tunable red emission was obtained by incorporated a rubrene derivative into both NPB and Alq<sub>3</sub> hosted device. The red

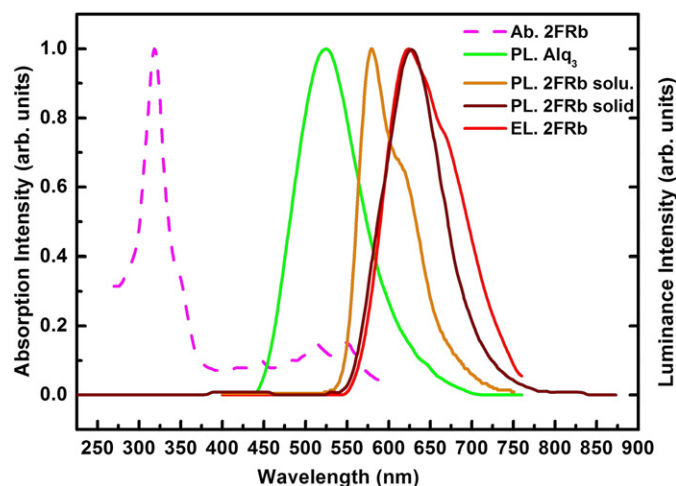


Fig. 6. The PL and absorption spectra of 2FRb in CH<sub>2</sub>Cl<sub>2</sub> solutions and PL spectra of neat Alq<sub>3</sub> and 2FRb film and EL spectra of 2.4 wt.% 2FRb doped Alq<sub>3</sub> device.

emission could be adjusted from 560 nm to 622 nm in Alq<sub>3</sub> hosted device while from 580 nm to 607 nm in NPB hosted devices by increasing doping concentration. Alq<sub>3</sub> hosted device shows better performances, it has a maximum luminance of 3100 cd/m<sup>2</sup>, a maximum efficiency of 2.42 cd/A and a pure red emission peaking at 622 nm with CIE coordinates of (0.65, 0.35) at very high doping concentration of 3.2 wt.%, respectively. The luminance and efficiency saturated at high doping concentration with pure red emission. This indicates that the bipolar 2FRb was a promising red emitter for the potential applications in organic light emitting devices.

## References

- [1] J. Kido, M. Kimura, K. Nagai, *Science* 267 (1995) 1332.
- [2] T.H. Liu, C.Y. lou, C.H. Chen, *Appl. Phys. Lett.* 83 (2003) 5241.
- [3] V. Bulovic, A. Shoustikov, M.A. Baldo, E. Bose, V.G. Kozlov, M.E. Thompson, S.R. Forrest, *Chem. Phys. Lett.* 287 (1998) 455.
- [4] C.H. Chen, C.W. Tang, J. Shi, P. Klubek, *Macromol. Symp.* 125 (1997) 49.
- [5] R.H. Young, C.W. Tang, A.P. Marchetti, *Appl. Phys. Lett.* 80 (2002) 874.
- [6] B.W. D'Andrade, S.R. Forrest, *Adv. Mater.* 16 (2004) 1585.
- [7] H. Mattoussi, H. Murata, C.D. Merritt, Y. Iizumi, J. Kido, Z.H. Kafafi, *J. Appl. Phys.* 86 (1999) 2642.
- [8] H. Murata, C.D. Merritt, Z.H. Kafafi, *IEEE J. Sel. Top. Quant.* 4 (1998) 119.
- [9] Y. Hamada, T. Sano, K. Shibata, K. Kuroki, *Jpn. J. Appl. Phys.* 34 (1995) 824.
- [10] Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, *Appl. Phys. Lett.* 75 (1999) 1682.
- [11] D.J. Fatemi, H. Murata, C.D. Merritt, Z.H. Kafafi, *Synthetic. Met.* 65 (1997) 1225.
- [12] Y. Sato, T. Ogata, S. Ichinosawa, Y. Murata, *Synthetic. Met.* 91 (1997) 103.
- [13] T.H. Liu, C.Y. lou, C.H. Chen, *Appl. Phys. Lett.* 85 (2004) 4304.
- [14] Hu Zhizhi, Masaru Kimura, Zhang Zhiqiang, Lei Peng, China Patent, No.1418858, 21 May. 2003.