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Letter

Red electroluminescent devices based on rubrene derivative in 4,4'-*N,N'*-dicarubreneazole-biphenyl host and its application in white light emitting device for lighting purpose

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ABSTRACT

A rubrene (Ru) derivative, 2-formyl-5,6,11,12-tetraphenyl-naphthacene (2FRu) was synthesized and was used as red dopant in *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) host in organic light-emitting device (OLED) that offers an emission peak at ~598 nm and a current efficiency of 2.12 cd/A. The red emitter was also used to fabricate a white OLED (WOLED), in which 2FRu, tris-(8-hydroxyquinoline) aluminum (Alq₃) and NPB contribute to the red, green and blue emissive components, respectively. As a result, a high color rendering index of 89.8, CIE coordinates of (0.33, 0.33) at 11 V as well as a maximum luminance of 5000 cd/m² and a luminance efficiency of 4.72 cd/A were obtained. The performances suggest its potential applications for solid-state lighting. Also, the design and electroluminescent processes of the WOLED based on 2FRu were also discussed.

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1. Introduction

Organic light-emitting devices (OLEDs) have attracted much more attention due to their potential applications in flat-panel displays and especially in solid-state lighting [1–3]. One of the key developments in the process of OLED technology can be attributed to the discovery of the host-guest doped emitter system by doping highly fluorescent guests in proper hosts, which can effectively improve the efficiency and stability of the device. For red-emitting materials, doped emitter system is a common method solving the problem of serious intermolecular aggregation of the guest molecules in solid-state due to its polarity or highly π -conjugated nature [4]. Pyran-containing energy-transfer-type compounds, such as, 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-8-yl)vinyl]-4H-pyran (DCM2) [5] and 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetra-methyljulolidyl-9-enyl)-4H-pyran (DCJTb), were mostly used as red dopant in tris(8-hydroxyquinoline) aluminum (Alq₃) host [6], have been widely studied and regarded as the most important red dopants for OLED applications. However, the performance of devices with

such red emitters is still insufficient, such as, charge-induced fluorescence quenching and lower efficiency [7]. Also, hole-cations sometimes form easily so as to the operation efficiency and stability of the device were lowered. Besides choosing other proper hosts or co-hosted system for red dopants, molecular modification of charge-trap-type compounds, like rubrene (Ru), would be another method to improve the electroluminescent (EL) performances of red emitters. Ru is a common well-known efficient yellow dopant [8–10] for that it has some attractive properties, such as near unity photoluminescent (PL) quantum efficiency and bipolar character [11], and it also can be used as an assistant dopant to overcome concentration quenching and further to improve the efficiency and operation stability [12–15] of the devices. In this article, a rubrene derivative, 2-formyl-5,6,11,12-tetraphenyl-naphthacene (2FRu), was home synthesized and incorporated into the hole transport *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) host. Red EL peaks at ~598 nm as well as a maximum efficiency of 2.12 cd/A was achieved without deteriorating other excellent properties of Ru. White OLED (WOLED) based on the red emitter was also fabricated which offers high illumination quality, i.e., a color rendering index (CRI) of 89.8, Commission Internationale de L'Eclairage (CIE) coordinates of $x = 0.33$, $y = 0.33$ at 11 V, suggesting its potential application in lighting.

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2. Experimental

2FRu was synthesized and purified in our lab and other chemicals were commercially purchased without further purification. All materials were deposited in vacuum onto a pre-cleaned indium tin oxide (ITO)-coated glass substrate with sheet resistance of $20 \Omega/\text{sq}$. The substrates were routinely cleaned by ultrasonic solvent bath and then exposed to an UV-ozone ambient prior to loading in a vacuum chamber. All organic layers were deposited in succession without breaking vacuum ($\sim 3 \times 10^{-4}$ Pa). Thermal deposition rates of organic materials, LiF, and Al were ~ 1 , ~ 1 , and 10 \AA/s , respectively. PL absorption spectra and emission spectra and of Ru and 2FRu in CH_2Cl_2 solutions, PL spectrum of the neat NPB film EL spectra and CIE coordinates were measured with a Hitachi MPF-4 fluorescence spectrophotometer. Also, the correlated color temperature (CT) and CRI were obtained in Hitachi MPF-4 fluorescence spectrophotometer by the calculation of the spectra. The data of luminance-current-voltage ($L-I-V$) were measured with a 3645 dc power supply combined with a 1980A spot photometer and were recorded simultaneously with measurement. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of the 2FRu were determined with a cyclic voltammeter and calculated with the absorption spectra. All measurements were performed at room circumstance without encapsulation.

Two series of devices were fabricated with the following structure:

Device 1: ITO/CuPc(5 nm)/NPB(40 nm)/NPB:2FRu(x wt%, 30 nm)/TPBi (50 nm)/LiF(1 nm)/Al(200 nm), here $x = 0.5, 0.8, 1.0, 1.5, 2.0, 2.5$ and 3.0 , respectively.

Device 2: ITO/CuPc (5 nm)/NPB (40 nm)/NPB:2FRu(0.8 wt%, 8 nm)/NPB (2 nm)/(BCP) (4 nm)/Alq₃ (40 nm)/LiF(1 nm)/Al (200 nm), here, CuPc is copper phthalocyanine for helping holes injection, TPBi is 1,3,5-tris(2-*N*-phenylbenzimidazolyl) benzene as hole-blocker and electron transporter, and BCP is 4,4'-*N,N'*-dicarbazole-biphenyl, functions as partial hole-blocker. Alq₃ layer functions as green emitter and electron transporter. 2-nm neat thin NPB layer inserted between the doped and BCP layers was to confine excitons within the emitting layer.

3. Results and discussion

Insert of Fig. 1a depicts the chemical structure of 2FRu that was synthesized by introducing a formyl group on tetracene backbone

of Ru molecule, not functioning as the chromophore, but adjusting the conjugation degree of Ru molecule. The LUMO and HOMO levels of 2FRu molecule were found to, respectively be at around 3.25 and 5.36 eV with a band gap of 2.11 eV, which is narrower than that of Ru for 0.1 eV, indicating that the conjugation of 2FRu was increased compared with that of Ru molecule. Its chemical structure was confirmed by ¹H-nuclear magnetic resonance (NMR), mass spectrum and element analysis. The sublimated product has the same chemical structure by NMR analysis indicating that the material keeps stable during the vacuum sublimation process. The EL emission spectra of the devices doped with different weight contents of 2FRu are indicated in Fig. 1. A maximum current efficiency of 2.12 cd/A of the red device was observed by using a doping concentration of 1.5 wt%, which is about the same with the efficiency of the device with 0.7% doped rubrene reported by our group [16].

Fig. 1a displays that EL emission peak was tuned from 560 nm from rubrene to 598 nm from 2FRu and does not shifted with varying concentration indicating that the conjugation was increased by the molecular modification and the main luminance mechanism should be the charge trapping [8]. There also is a weak emission peak at ~ 440 nm originated from NPB due to incomplete energy transfer from NPB host to 2FRu dopant when the doping concentration lower than 1.5 wt%. Fig. 1b and its insert show the EL spectra and the evolution of the corresponding CIE coordinates of the devices with doping concentration continuously lowering from 1.5 to 0.5 wt%. We can see that the two emission peaks exhibit a gradual comparable intensity and emissive color shift from bluish white to pink white when dopant concentration further lowers to 0.5 wt%, as shown in its spectral figure, that is, the blue emissive band intensity decreases as the dopant concentration rises from 0.5 to 1.5 wt%. The evolution of the corresponding CIE coordinates is indicated in the inset, it means that the white emission is short of green component. Device 2 with three-elements was fabricated by introduction of Alq₃ as green emitter.

Fig. 2 shows the absorption spectra, PL spectra of Ru and 2FRu in CH_2Cl_2 solutions and EL spectra of neat NPB film. We notice that both the absorption spectra and the PL spectral peaks of 2FRu shifted to longer wavelength and have the same spectral profiles as compared with that of Ru, indicating that the introduction of formyl group into Ru molecule increased the conjugation degree of Ru molecule. Also, smaller spectral overlapping between the absorption spectrum of 2FRu and emission spectrum of NPB film indicates that the main luminescence mechanism is charge

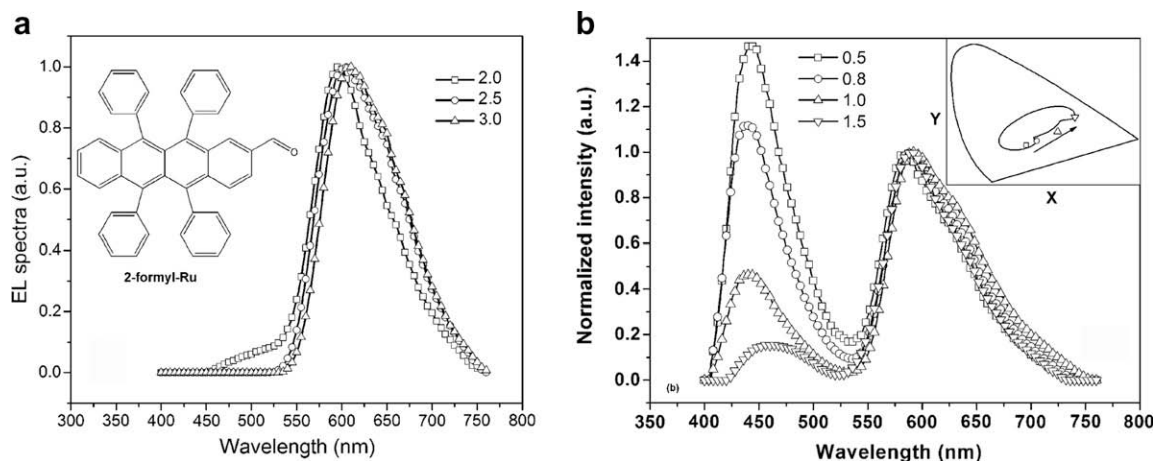


Fig. 1. EL spectra of devices with stepping doping content of Device 1. Inset of (a): the chemical structure of 2FRu and inset of (b): the corresponding CIE evolution.

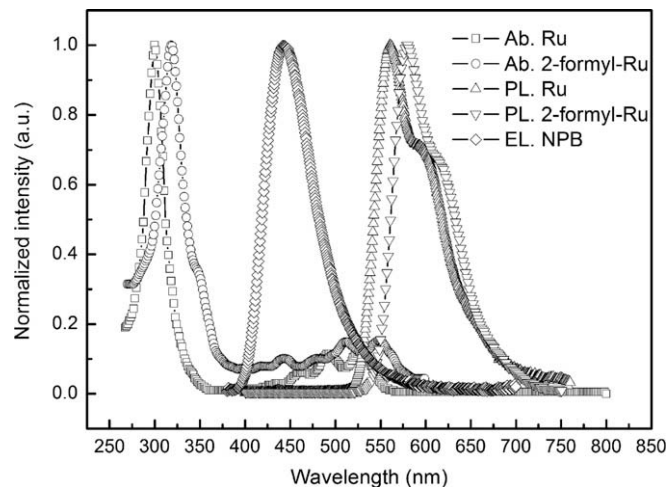


Fig. 2. The PL absorption spectra, emission spectra of Ru and 2FRu in CH_2Cl_2 solutions and EL spectra of neat NPB film.

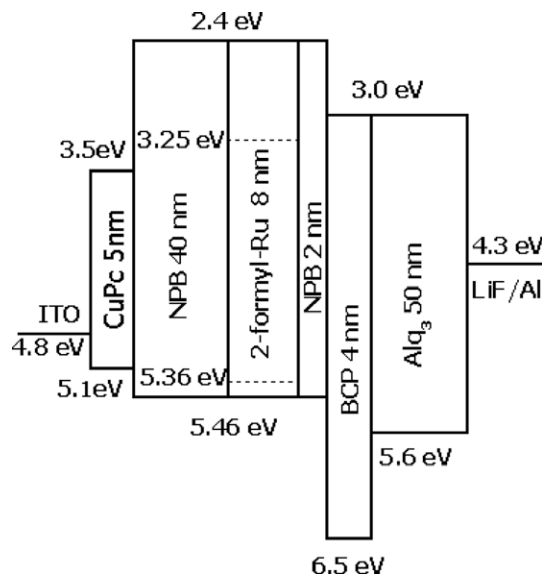


Fig. 4. Schematic energy level diagram of WOLED for lighting purpose.

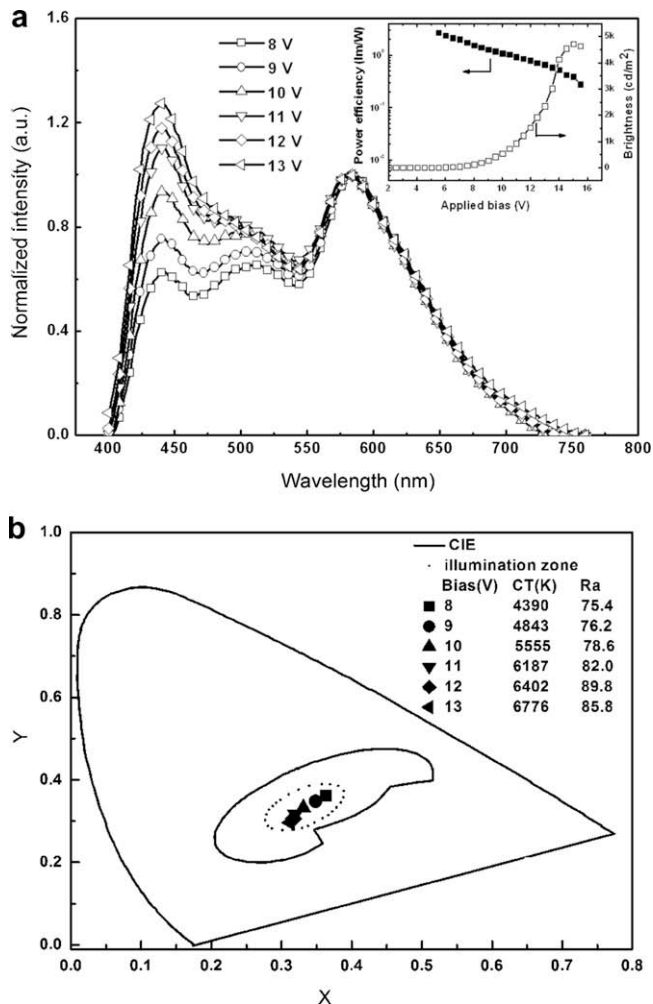


Fig. 3. (a) Normalized EL spectra under different biases of Device 2, inset: power efficiency–luminance–voltage characteristics and (b) evolution of the corresponding CIE coordinates.

trapping in EL process, which is identical to Ru doped NPB emitter based device.

Fig. 3a indicates the forward bias dependence of the EL spectrum of Device 2. Compared with Fig. 1b, there exists another emission peak at ~ 530 nm beside two peaks from NPB host and 2FRu dopant, which is ascribed to the emission from Alq_3 , indicating that above structure design of the device works and we get a three-element white emission. From the figure, we can see that the emission intensities of both the blue and the green sub-bands are lower than that of the red one from 2FRu under biases lower than 10 V, while the three sub-bands composing white spectral band tend synchronously variety at biases higher than 10 V, but the blue emission from the 2 nm NPB layer also appears when the bias increases, as a result, the broadband white light emission was obtained. The optimized device exhibits a high CRI of 89.8, CIE coordinates of (0.33,0.33) at 11 V (see Fig. 3b). Inset of Fig. 3a shows the power efficiency–luminance–bias characteristics of the WOLED, a maximum luminance of 5000 cd/m^2 and a luminance efficiency of 4.72 cd/A were harvested, respectively. Furthermore, when forward bias increases from 8 to 13 V, the correlated color temperature (CCT) changes from 4390 to 6776 K, which overlaps standard CCT area and the CRI changes from 75.4 to 85.8, as shown in Fig. 3b, this expresses that the WOLED behaves relatively color stability over driving voltages from 8 to 13 V. It is believed that 2-nm NPB, BCP and Alq_3 layers in the WOLED play crucial roles in achieving the broadband white emission.

Fig. 4 indicates the schematic energy level diagram of WOLED, together with Fig. 1 and Fig. 2, the EL process and working mechanism might be understood as follows. The emission peak of 2FRu did not shift with doping concentration, the PL and absorption spectra nearly have the same profile with that of Ru, and little spectral overlap with NPB host improved that the EL mechanism of the device is charge trapping. As the bias is below 10 V, more injected electrons and holes were trapped on the 2FRu molecules and stronger red emission and weaker blue emission occurred. While bias is higher than 10 V, charge carriers trapped on 2FRu molecules could be saturated so that some holes would travel through the doping emitter layer to reach the interface between the neat thin NPB and BCP layers, leading to increase in the blue emission for the carrier recombination within the neat NPB layer. In other words, the blue emission in the WOLED comes, respectively from the host and the neat NPB layers.

4. Summary

In summary, due to introduction of formyl group on the position two of Ru molecule a red-emitting 2FRu with a larger π -conjugated degree was obtained, and the emission spectrum shifts to longer wavelength zone, red EL was achieved when 2FRu was doped into NPB host a 598 nm emission peak and a peak efficiency of 2.12 cd/A were achieved, under which a WOLED with lighting nature was constructed, which has a CRI of 89.8, CIE coordinates of (0.33,0.33) at 11 V as well as a maximum luminance of 5000 cd/m² and a current efficiency of 4.72 cd/A, respectively. It is a potential candidate for lighting applications although the efficiency needs to be further improved.

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