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Red Organic Light Emitting Diodes with Assist Dopant 2, 5, 8, 11-Tetra-Tertbutylperylene

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Abstract: A red organic light emitting device with host 9, 10-di-(2-naphthyl) anthracene (ADN) and red dopant 4-(dicyanomethylene)-2-t-butyl-6(1, 1, 7, 7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) and assist blue dopant 2, 5, 8, 11-tetra-tertbutylperylene (TBPe) was fabricated, and 4,4',4''-tris[2-naphthyl(phenyl)amino] triphenylamine (2TNATA), 4, 4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), tris-(8-hydroxyquinoline) aluminum (Alq₃) were used as hole injection, hole transportation, electron transportation materials, respectively. The results show that ADN doped with DCJTB can realize red emission as well, and the use of TBPe as assist dopant effectively enhance the device luminous efficiency, yet almost have no effects on CIE coordinates. Additionally, devices with 2% TBPe (mass fraction) appear optimum luminous efficiency and highest temperature increase rate.

Key words: red OLEDs; TBPe; DCJTB; efficiency; temperature

2, 5, 8, 11-Tetra-Tertbutylperylene 作为辅助掺杂剂的红色有机电致发光二极管

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摘 要: 制备了采用 9, 10-di-(2-naphthyl)anthracene (ADN) 作为主体, 4-(dicya-nomethylene)-2-t-butyl-6(1, 1, 7, 7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) 作为红色发光中心, 2, 5, 8, 11-tetra-tertbutylperylene (TBPe) 作为辅助掺杂剂的红光有机电致发光器件。4, 4', 4''-tris[2-naphthyl(phenyl)amino]triphenylamine (2TNATA) 用作空穴注入材料, 4, 4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), tris-(8-hydroxyquinoline) aluminum (Alq₃) 用于空穴和电子传输。实验结果表明, 掺有 DCJTB 的 ADN 也可实现红色发光, 掺入 TBPe 作为辅助掺杂, 可以提高该红光器件的效率, 但几乎不改变器件色坐标。此外, 2% TBPe (质量分数) 作为辅助掺杂的器件表现出最佳的流明效率和最大升温速率。

关 键 词: 红色有机电致发光二极管; TBPe; DCJTB; 效率; 温度

中图分类号: TN 383⁺.1 **文献标识码:** A

1 Introduction

The ideal of using assist dopant was applied by Yuji Hamada *et al* in 1999, 4-Dicya-nomethylene-2-methyl-6-[2-(2, 3, 6, 7-tetra-hydro-1H, 5H-benzo [ij]quinolizin-8-yl)vinyl]-4H-pyran(DCM2) and 5,6, 11,12-tetraphenyl-naphthacene(rubrene) were simultaneously doped into tris-(8-hydroxyquinoline) aluminum(Alq_3) to get a pure red organic light emitting device. It is believed that injected holes and electrons in Alq_3 transfer to rubrene molecular and recombine, then excitation energy is efficiently transferred to DCM2 due to the closeness of their HOMO(highest occupied molecular orbital) and LUMO(lowest unoccupied molecular orbital)^[1]. Since then similar investigations had been performed, like Alq_3 : Quinacridone (QAD, red fluorescent dye) : 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) by Jing Feng *et al*, here QAD plays a role of excitation energy tranfer^[2]. Alq_3 : 10-(2-benzothiazolyl)-2, 3, 6, 7-tetrahydro-1, 1, 7, 7,-tetramethyl-1H, 5H,11H-(1)-benzopyrroprano-(6,7-8-i,j) quino-lizin-11-one (C545T, green fluorescent dye) : DCJTB by Jiangshan Chen, Dongge Ma^[3], where C545T did not emit but assist carrier trapping from Alq_3 to DCJTB.

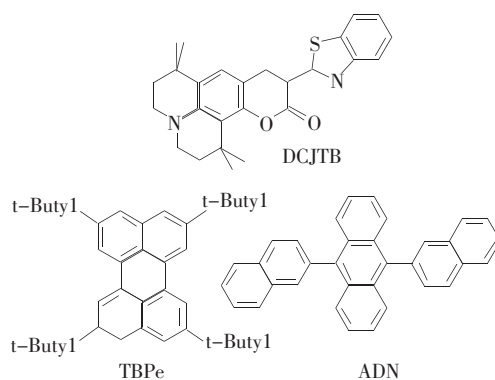
9, 10-di-(2-naphthyl)anthracene (ADN) is found to be ambipolar with carriers mobility ranged from $(1 \sim 4) \times 10^{-7} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (under $0.5 \sim 0.8 \text{ MV/cm}$)^[4], and 2, 5, 8, 11-tetra-tertbutylperylene (TBPe) is usually doped into it to generate a good blue emission^[5]. There were few investigations on the ADN host to obtain a red emission, and almost no reports about TBPe as assist dopant in red devices, so we focus the two points in this study.

This study proposed a red device with host ADN and assist dopant TBPe, emitter ADN : TBPe : DCJTB with different TBPe ratio was investigated to show how it works. The study used a device structure ITO/2TNATA/NPB/Emitter/ Alq_3 /LiF/Al, and provided details

about efficiency enhancement and surface temperature characteristics with respect to variation of TBPe concentration, also an analysis about the inner emission mechanism was given.

2 Experiments

Indium Tin Oxide(ITO) coated glass with a sheet resistance $20 \Omega/\square$ was cleaned via detergent, acetone, anhydrous ethanol successively and followed by 10 min oxygen plasma treatment, then ITO glass was transferred into the vacuum chamber (about $3 \times 10^{-4} \text{ Pa}$) for film deposition. 4, 4', 4''-tris [2-naphthyl (phenyl) amino]triphenylamine (2TNATA) was used as the hole injection material, meanwhile 4, 4'-bis [N-(1-naphthyl)-N-phenylamino] biphenyl (NPB) and tris-(8-hydroxyquinoline) aluminum (Alq_3) were evaporated to transport the hole and electron respectively. Two kinds of dopants 2, 5, 8, 11-tetra-tertbutylperylene (TBPe) and 4-(dicyanomethylene)-2-t-butyl-6(1, 1, 7, 7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) were simultaneously doped into the host 9, 10-



(a) Chemical structure of main materials

LiF/Al(0.5 nm+100 nm)
Alq_3 (20 nm)
ADN:TBPe:DCJTB(20 nm)
NPB(25 nm)
2TNATA(25 nm)
Glass/ITO

(b) Configuration of red devices prepared

Fig. 1 Chemical structures of main materials and configuration of the red devices prepared

di-(2-naphthyl) anthracene (ADN) via thermal evaporation to form a single light emitting layer, and LiF/Al was prepared as a composite cathode without break vacuum. The chemical structure of main materials and overall structure of the device are shown in Fig. 1. The evaporate rate for organic materials was about 0. 2 nm/s and rates ranged 1 nm/s for metals, the active areas was about 14 mm×15 mm.

The electroluminescence spectra were measured by PMS-80 (from EVERFINE PHOTO-E-INFO CO., LTD), the *I-V-L* characteristics were tested using ST-900 spectrophotometer, and current-voltage meters under room temperature and in ambient atmosphere, additionally, temperature-voltage characteristics of devices were tested via a thermocouple contacting on the surface of glass.

3 Results and Discussion

The *I-V-L* characteristics of devices with different TPBe(0%~6%, mass fraction) and a fixed DCJTB(6%) concentration are shown in Fig. 2 below. In Fig. 2(a), it can be seen that all devices showed typical trend of a diodes, 0%, 6% devices have higher current density, and that of 2%, 4% devices is lower.

In Fig. 2(b), the luminance of 2%, 4% devices is much higher than 0%, 6% devices. Taking the *I-V* characteristics into consideration, it can be found that 2%, 4% devices have higher luminous efficiency because luminous efficiency can be expressed as $\eta = S \times L / I(S, L, I$ corresponding to active area, luminance, current,

respectively).
In order to put it specifically, luminous efficiency and Commission Internationale de L'Eclairage (CIE) coordinates of devices with 6% DCJTB and 0% , 2%, 4%, 6% TBPe are given in Table 1. Obviously, the means of doping TBPe lead to a overall increase in turn-on vol-tage, yet devices efficiency is increased simultaneously (20 mA/cm² and 120 mA/cm²). All devices almost showed similar CIE coordinates, resulting from high DCJTB concentration in emitter ADN:TBPe:DCJTB.

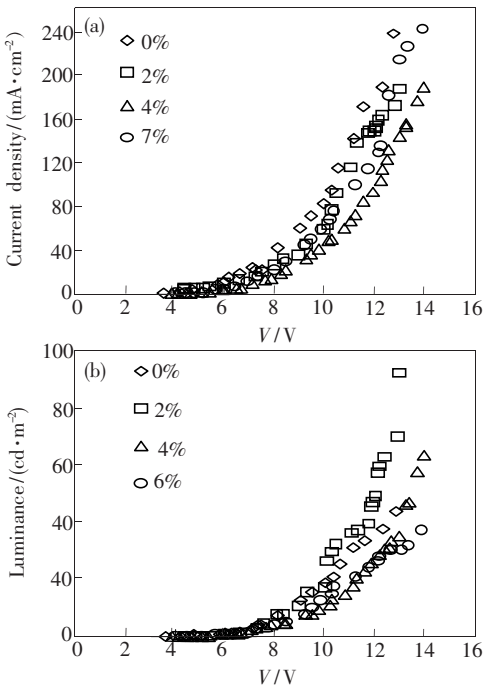


Fig. 2 Current density-luminance-voltage characteristics of devices with different TBPe concentration, (a) Current density vs. voltage; (b) Luminance vs. voltage.

The dependence of efficiency on TBPe concentration is surely related to the emitting layer

Table 1 luminous efficiency and CIE coordinates of devices with 6% DCJTB and 0%, 2%, 4%, 6% TBPe(mass fraction)						
DCJTB(%)	TBPe(%)	V _{turn on} (V)	η_{20} (cd/A)	η_{120} (cd/A)	η_{max} (cd/A)	CIE(x,y)0.06
6	0	3.57	1.81	2.18	2.28	(0.574 5,0.413 0)
6	2	4.39	2.13	3.18	3.88	(0.563 0,0.419 2)
6	4	4.16	2.15	2.55	2.78	(0.551 5,0.426 4)
6	6	4.08	1.67	2.03	2.32	(0.555 4,0.423 8)

η_{20} and η_{120} is the luminous efficiency under 20 mA/cm² and 120 mA/cm², respectively;
 η_{max} is maximum efficiency, CIE(x,y)0.06 is CIE coordinates tested under 0.06 A.

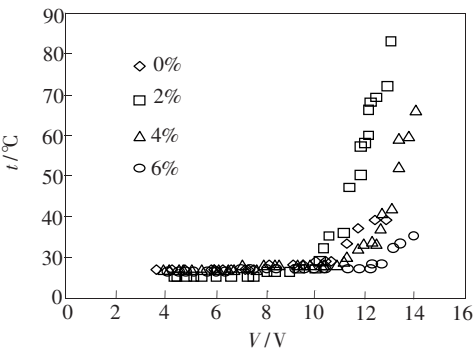


Fig. 3 Curves of temperature *vs.* voltage

ADN:TBPe:DCJTB system, not other functional layers, for the dopant concentration do not affect the other functional layers except the light emitting layer. Devices with TBPe show higher efficiency, Yuji Hamada et al attributed the efficiency enhancement to assist dopant-induced energy transfer effect, but there were little further investigations. The concentration quenching effect may result to low brightness and efficiency of 6% TBPe device, so there is a optimum TBPe ratio in the emitter.

Besides the efficiency characteristics, temperature-voltage characteristics of devices with 6% DCJTB and 0%, 2%, 4%, 6% TBPe are given in Fig. 3. Apparently, the 2%, 4% devices have higher slope of T - V curves when comparing to the 0%, 6% devices, and 2% device exhibites a maximum temperature increase rate. It seems the temperature increase of device depends on the TBPe concentration as well. There are little investigations on the temperature characteristics of OLEDs^[6], but it is sure that the temperature is related to the devices efficiency enhancement. Taking the I - V curves into consideration, devices with 2%, 4% TBPe obtain lower electrical power ($W=I\times V$) under the same voltage (12 V for example), yet luminous efficiency is higher than 0%, 6% TBPe devices. Considering $\eta_p = \Pi \times \eta_c / V$ (η_p and η_c relate to power efficiency and luminous efficiency, respectively), obviously, power efficiencies of devices with 2%, 4% TBPe are higher than 0%, 6% devices as well. In this

case, the non-emission electrical powers $(1-\eta_p)\times W$ for 2%, 4% devices are lower than 0%, 6% devices, hence the high temperature slope of 2%, 4% devices are not induced by total non-emission electrical power. Here we attribute the high temperature slope to inner carriers recombination. An optimum TBPe concentration leads to high recombination ratio, so more excitons are generated per unit time in this optimum device and amount of heat correspondingly increase in unit time when excitons decay, so temperature upgrade quickly in a optimal devices.

Additionally, it is noted to point out that the temperature difference appears at about 10 V, not from the beginning. This is because of the total electrons and holes entering the light emitting layer, it is not sufficient under low voltage and turns more when higher voltage applied, correspondingly, all devices show no temperature distinction under low voltage and obvious difference under higher voltage for the distinct efficiency.

The electroluminescence spectra of devices with 0%, 2%, 4%, 6% TBPe and 6% DCJTB

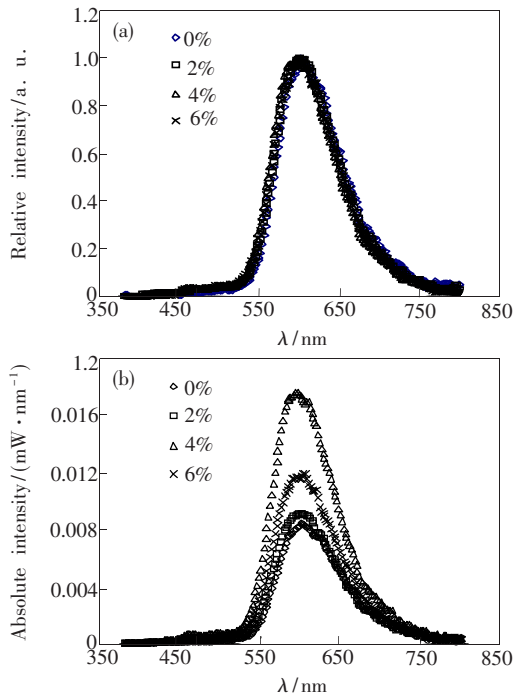


Fig. 4 EL spectra characteristics of devices with different TBPe concentration under 0.06 A. (a) Relative spectra of devices; (b) Absolute spectra of devices.

under a current of 0.06 A are shown in Fig. 4. Obviously, the TBPe concentration almost do not affect the relative intensity of devices but vitally do when considering the absolute intensity. The peak of 0% TBPe in ADN:TBPe:DCJTB system locates in about 600 nm, it doesn't shift with TBPe ratio increasing, and there is a small peak around 450 nm. As for absolute intensity of spectra, the apparent difference in intensity indicates the dependence of TBPe concentration in the emitting layer, yet it differs from descriptions above, here the 4% exhibits a maximum value rather than the 2% device.

The difference comes from current driving style here, it is easier to understand the difference when Fig. 2(a) is taken into consideration. The small peak around 450 nm comes from ADN or TBPe, indicating that there are few carriers recombination on ADN or TBPe molecular.

Now we turn to discuss the efficiency enhancement. Cascade energy levels may exist in this ADN:TBPe:DCJTB system, that is, the LUMO for TBPe located between that of ADN and DCJTB, and the same situation for HOMO level. Consequently, there are three explanations to efficiency dependence on TBPe dopant:

(1) Injected holes and electrons enter HOMO and LUMO of ADN and recombine, leading to excitation of ADN molecular. The excitations energy transfers to DCJTB by the medium of TBPe, and DCJTB molecular emits light. In this case, TBPe molecular are energy transfer medium;

(2) Injected holes and electrons transfer from HOMO and LUMO of ADN to that of TBPe, recombination occurs on TBPe moleculars. The excitations energy TBPe is transferred to DCJTB molecular and TBPe plays a role of energy transfer as well;

(3) Holes and electrons transfer to HOMO and LUMO of DCJTB step by step, recombination occurs on DCJTB molecular and light is emitted. Here TBPe molecular are carriers transfer medium.

It is sort of tough to analyze which one dominates the light emission without other investigations on this system, but there are some helpful details. Comparing to devices without TBPe, devices with it have higher turn-on voltage. Carriers recombination occurs on DCJTB moleculars with no TBPe, and recombination happens on TBPe molecular then excitation energy transfer to DCJTB in ADN:TBPe:DCJTB, for TBPe may have wider bandgap than DCJTB. In a colorful spectra of the devices (not given), once TBPe is doped into ADN:DCJTB, the small peak appears, so there may exist incomplete energy transfer from TBPe to DCJTB. Further study on this system is in need to discuss the inner mechanism.

4 Conclusions

From the experiments and discussions above, three conclusions can be reached:

(1) Red emission can be obtained by doping DCJTB to host ADN, yet the device display low efficiency.

(2) The emitter ADN:TBPe:DCJTB shows high luminous efficiency than emitter ADN:DCJTB, TBPe almost did not emit but functioned as a energy transfer or carriers transporting medium.

(3) The optimum TBPe doping concentration for emitter ADN:TBPe:DCJTB is 2% (mass fraction), and the emitter ADN:(2%)(TBPe):(6%)DCJTB show highest temperature increase slope among 0%, 2%, 4%, 6% TBPe devices.

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可与国际单位制并用的我国法定计量单位

量的名称	单位名称	单位符号	换算关系和说明
时间	分	min	1 min=60 s
	[小]时	h	1 h=60 min=3 600 s
	日,(天)	d	1 d=24 h=86 400 s
	[平面]角	[角]秒	1 ''=(1/60) '=(π /648 000) rad
		[角]分	1 '=(1/60) °=(π /10 800) rad
质量	度	°	1 °=(π /180) rad
	吨	t	1 t=10 ³ kg
	原子质量单位	u	1u≈1.660 540×10 ⁻²⁷ kg
旋转速度	转每分	r/min	1 r/min=(1/60) s ⁻¹
体积	升	L,(l)	1 L=1 dm ³ =10 ⁻³ m ³
能	电子伏	eV	1 eV≈1.602 177×10 ⁻¹⁹ J
级差	分贝	dB	
线密度	特[克斯]	tex	1 tex=10 ⁻⁶ kg/m=1 g/km
面积	公顷	hm ²	1 hm ² =10 000 m ²
长度	海里	n mile	1 n mile=1 852 m(只用于航行)
速度	节	kn	1 kn=1 n mile/h=(1 852/3 600) m/s(只用于航行)