混合蓝色和绿色发射的高亮度白色有机电致发光器件

马 涛[1]　　蒋亚东[1]　　于军胜[1,*]　　娄双玲[1]　　李 璐[1]　　张 清[2,*]

(¹ 电子科技大学光电信息学院, 电子薄膜与集成器件国家重点实验室, 成都　610054;
² 上海交通大学化学化工学院高分子科学与工程系, 上海　200240)

摘要：　使用星形六苯芴类新材料 1,2,3,4,5,6-hexakis(9,9-diethyl-9H-fluoren-2-yl)benzene (HKEthFLYPh)分别制备了三种不同结构的有机电致发光器件. 在结构为 indium-tin oxide (ITO)/NPB (40 nm)/HKEthFLYPh (10 nm)/Alq₃ (50 nm)/Mg:Ag (200 nm)的器件中, 获得了两个电致发光谱峰分别位于 435 和 530 nm 处的明亮白光. HKEth-FLYPh 是能量传输层; *N,N′*-bis-(1-naphthyl)-*N,N′*-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB)是空穴传输层和蓝色发光层; tris(8-hydroxyquinoline)aluminum (Alq₃)是电子传输层和绿色发光层. 结果表明, 当驱动电压为 15 V 时, 器件的最大亮度达到 8523 cd·m⁻²; 在 5.5 V 时, 器件达到最大流明效率为 1.0 lm·W⁻¹. 在电压为 9 V 时, CIE 色坐标为(0.29, 0.34). 此外, 通过改变 HKEthFLYPh 层的厚度, 发现蓝色发射的相对强度随着 HKEthFLYPh 层厚度的增加而增强.

关键词：　白色有机电致发光器件；　星形六苯芴；　HKEthFLYPh；　能量传递
　　中图分类号：　O644

Bright White Organic Light-Emitting Diode Mixed Blue and Green Emission

MA Tao[1]　　　JIANG Ya-Dong[1]　　　YU Jun-Sheng[1,*]　　　LOU Shuang-Ling[1]　　　LI Lu[1]　　　ZHANG Qing[2,*]

(¹*State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu　610054, P. R. China*;　²*Department of Polymer Science and Engineering, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai　200240, P. R. China*)

Abstract：　Double-layer and triple-layer organic light-emitting diodes (OLEDs) were fabricated using a novel star-shaped hexafluorenylbenzene organic material, 1,2,3,4,5,6-hexakis(9,9-diethyl-9H-fluoren-2-yl)benzene (HKEthFLYPh) as an energy transfer layer, *N,N′*-bis-(1-naphthyl)-*N,N′*-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) as a hole-transport layer (HTL) and blue emissive layer (EML), and tris(8-hydroxyquinoline)aluminum (Alq₃) as an electron-transport layer (ETL) and green light-emitting layer. Bright white light was obtained with a triple-layer device structure of indium-tin-oxide (ITO)/NPB (40 nm)/HKEthFLYPh (10 nm)/Alq₃ (50 nm)/Mg:Ag (200 nm). A maximum luminance of 8523 cd·m⁻² at 15 V and a power efficiency of 1.0 lm·W⁻¹ at 5.5 V were achieved. The Commissions Internationale de L′ Eclairage (CIE) coordinates of the device were (0.29, 0.34) at 9 V, which located in white light region. With increasing film thickness of HKEthFLYPh, light emission intensity from NPB increased compared to that of Alq₃.

Key Words：　White organic light-emitting diode (WOLED);　Star-shaped hexafluorenylbenzene;
　　　　　　　　HKEthFLYPh;　Energy transfer

Since Tang and Vanslyke[1] from Eastman Kodak reported an organic light-emitting diode (OLED) with high efficiency in 1987, OLEDs have been developed as a new technology for next generation flat-panel displays because of their high luminance efficiency, low-power consumption, quick response time, and wide viewing angle.

High luminance and efficiency in red (R), green (G), and blue (B) OLEDs were obtained using a discrete emitting layer or by doping fluorescent and phosphorescent dyes into a host layer, and a full-color display can be achieved by integrating individual pixels of RGB emission. Another method to achieve a full-color display is to use color filter (CF) on white light OLEDs to change the emissive light into RGB color. The latter method is the popular way used in full-color liquid crystal displays (LCDs). Transferring existing color filter technology to an OLED display can greatly simplify the fabrication processing of a full-color OLED, since a white OLED (WOLED) is required. WOLEDS can also serve as illumination light sources and backlight panels of LCDs. For large-scale applications, WOLEDs are high-quality, low-cost, thin-film, flexible option, superior to inorganic light-emitting diodes (LEDs) or fluorescent lamps.

So far, a variety of methods have been proposed to achieve a WOLED, such as, (i) a multilayer device with blue, green, and red emissive layers[2], (ii) a doped device with a host material and blue, green, and red fluorescence dyes[3], (iii) a single-emission-layer device with white emission material[4], (iv) excimer and exciplex emissions[5], and (v) stacked structure[6]. Based on these techniques, we also did some work on WOLED, which is the most important factor for lighting application[7,8]. Recently, Sun *et al*.[9] reported that white emission from a blue fluorophore, a green and red phosphorescent dopant had maximum power of 37.6 lm·W^{-1}. However, it is still necessary to develop novel blue light-emitting material for white and full color devices.

On the other hand, compared to the linear-rod compounds used for optoelectronic devices including OLEDs, the device performance consisted of star-shaped material is significantly high, either as charge-transport material or as emitter, due to their tendency to form stable amorphous films with a relatively high T_g and improved thermal stability[10,11]. In this work, a bright WOLED was fabricated using a novel star-shaped hexafluorenylbenzene as an emissive assistance layer, and the electroluminescent (EL) properties were investigated.

1 Experimental

A novel star-shaped hexafluorenylbenzene 1,2,3,4,5,6-hexakis (9,9-diethyl-9H-fluoren-2-yl)benzene (HKEthFLYPh) with six-arm star shaped fluorene structure was synthesized in our group[12–14]. The organic materials of *N,N′*-bis-(1-naphthyl)-*N,N′*-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) and tris(8-hydroxyquinoline) aluminum (Alq$_3$) were both purchased from Sigma-Aldrich Co. NPB is a typical small molecular hole transporting material with a hole drift mobility on the order of 2.6×10^{-4} cm^2·V^{-1}·s^{-1}. Alq$_3$ has a high thermal and optical stability and charge-

transporting capability.

ITO-coated glass was employed as anode substrate with a sheet resistance of 10 Ω·$\square^{-1}$. Prior to the deposition of organic layers, ITO glasses were ultrasonically cleaned with detergent water, acetone, ethanol, and deionized water for 10 min at each step, and then dried with nitrogen gas. Afterwards, the glasses underwent an oxygen plasma treatment for ca 5 min in order to enhance the work function of ITO and thus improve its hole injecting capacity[15,16]. All the organic materials were deposited by conventional thermal evaporation in vacuum background at 3×10^{-4} Pa using the OLED-V organic multi-functional vacuum vapor deposition apparatus. Usually we start to evaporate the material at a rate of about 0.1 nm·s^{-1}. Organic film thickness is controlled by an oscillating quartz crystal thickness monitor. After the organic materials grew, the samples were transfered to another evaporator, an alloy of Mg and Ag with a proportion of 10:1 was deposited as the cathode using a mask, and the thickness was 200 nm.

In all the cases, the emitting area was 0.5 cm×0.5 cm, and the luminescent characteristics, such as current density−voltage (*J*−*V*), luminance−voltage (*L*−*V*) curves of the devices, were measured with KEITHLEY-4200 semiconductor characterization system and luminance meter ST-86LA at room temperature under ambient atmosphere. The EL emission spectra were recorded with a spectrophotometer OPT-2000.

Fig.1 shows the molecular structures of HKEthFLYPh, Alq$_3$, NPB, and device architectures.

2 Results and discussion

Fig.2 shows the absorption and photoluminescence (PL) spectra of NPB and HKEthFLYPh. It can be seen that there is a large overlap between HKEthFLYPh (375 nm) emission spectrum and NPB (355 nm) absorption spectrum. As we all know, energy transfer of both Förster and Dexter requires sufficient overlap of donor material emission spectrum with acceptor material absorption spectrum. Therefore, sufficient energy transfer from HKEthFLYPh to NPB can be expected.

For the comparison of EL properties of HKEthFLYPh, Alq$_3$, and NPB, three kinds of devices A, B, and C (as shown in Fig.1)
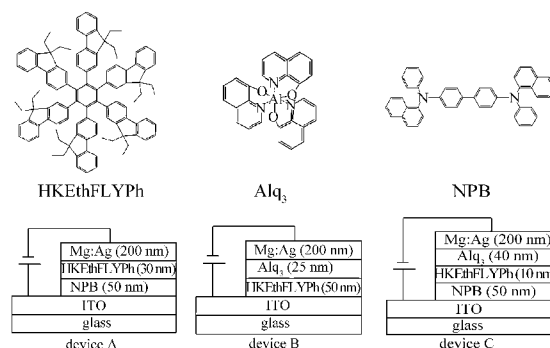

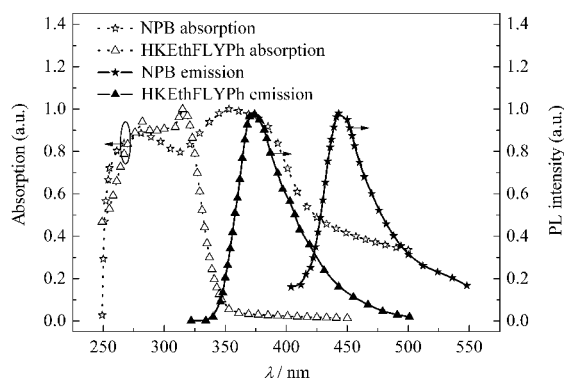**Fig.1 Molecular structures of the used materials and device architectures**

Fig.2　Absorption and PL spectra of HKEthFLYPh and NPB

Fig.4　EL spectra of device C at different driving voltages

were fabricated. Fig.3 shows the EL spectra of devices A, B, and C. It can be seen that the EL spectra of devices A and B only have one peak located at 435 and 530 nm, respectively. While the EL spectrum of device C has two peaks, which locate at 435 and 530 nm. This phenomenon can be explained from the different structures of devices A, B and C: in devices A and C, compared to the PL spectrum in Fig.2, it could be concluded that the peak at 435 nm in EL spectrum originated from the emission of NPB layer[17], and there was no emission of HKEthFLYPh. Accordingly, from HKEthFLYPh to NPB, complete energy transfer took place and HKEthFLYPh emission was thoroughly suppressed; in devices B and C, the EL spectral peak locates at 530 nm, which is attributed to the emission of Alq₃[18], and HKEthFLYPh just played the role as a hole transporting layer in device B.

　　The EL spectra of the triple-layer device ITO/NPB (40 nm)/ HKEthFLYPh (10 nm)/Alq₃ (50 nm)/Mg:Ag (200 nm) at various bias are shown in Fig.4. It can be seen that the device emits white light by the insertion of HKEthFLYPh and electron transporting (Alq₃) layers at the same time to enhance the emission of NPB (ca 435 nm), which has relatively stable chroma at the voltage ranging from 7 to 11 V. It can be seen that a significant broader EL spectrum ranging from 400 to 700 nm, which completely covers the totally broad wavelength region of visible light emission, is obtained. In addition, the EL spectrum contains two primary peaks at 435 and 530 nm, which are attributed to NPB and Alq₃ layers, respectively. The Commissions Interna-
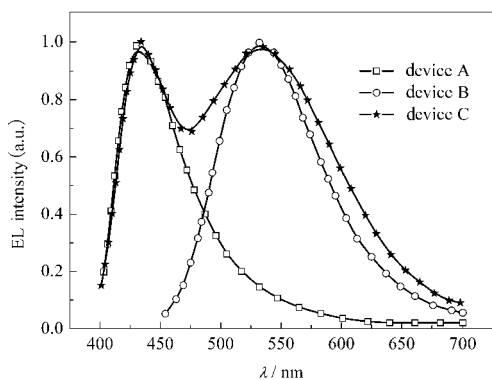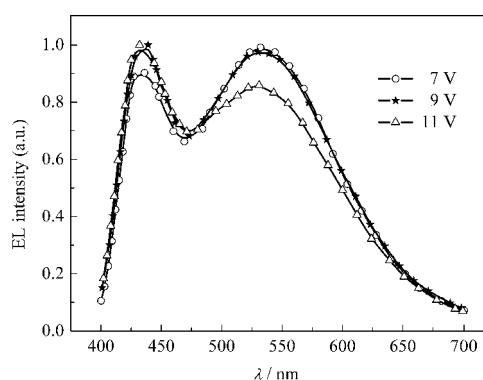
tionale de L′Eclairage (CIE) chromaticity coordinates are (0.29, 0.34), which obviously belong to white light emission. Importantly, this WOLED shows only a slight changing in EL spectrum with the enhanced driving voltage, e.g., the CIE coordinates change from (0.28, 0.35) at 7 V to (0.28, 0.33) at 11 V, and the peak intensity from the NPB layer increases compared to that of Alq₃ with increasing bias. This is mainly attributed to the change of charge carrier recombination region. This change is considered to be largely due to the impact of electric field on charge carrier mobility with the variation of applied voltage[19], and this phenomenon would arise only when the ratio of the number of electrons to that of holes increases with the driving voltage[20]. We could conclude that with increasing the voltage, the ability of HKEth-FLYPh transporting electrons is higher than that of holes, resulting in the enhancement of minor charge carries (electrons) injeted into NPB layer to recombine with major charge carries (holes) and causes an increase in NPB emission. Moreover, as driving voltage increases, free charge carriers to be injected into the HKEthFLYPh layer was enhanced resulting in the increased energy transfer from HKEthFLYPh to NPB. As a result, the relative intensity of blue light emission at 435 nm from NPB is higher.

　　The variation of luminance and current density with the applied voltage on the device C is shown in Fig.5. It indicates that the luminance and current density of device C increase with the augmentation of drive voltage, and in the range of high electric-field intensity, the current density has a relationship of exponen-
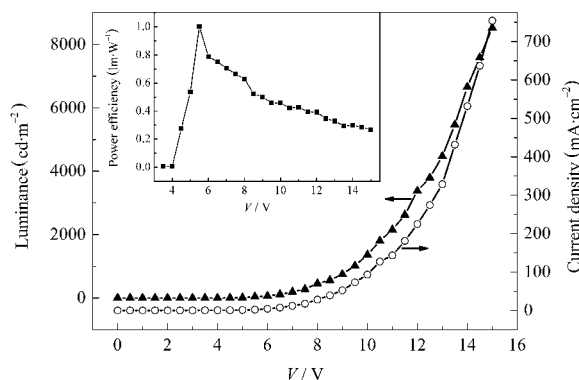

Fig.3　EL spectra of devices A, B, and C

Fig.5　Luminance–voltage–current density characteristic curves of device C

Inset shows power efficiency–voltage characteristic curve of device C.

Table 1   EL characteristics of devices A, B, and C

Device	V_{on}/V	J/(mA·cm^{-2})	L_{max}/(cd·m^{-2})	η_{max}/(lm·W^{-1})
A	4.0	1461	498	0.015
B	4.0	1160	517	0.029
C	3.5	753	8523	1.004

V_{on}: turn-on voltage; J: current density at 15 V; L_{max}: maximum luminance; η_{max}: maximum power efficiency
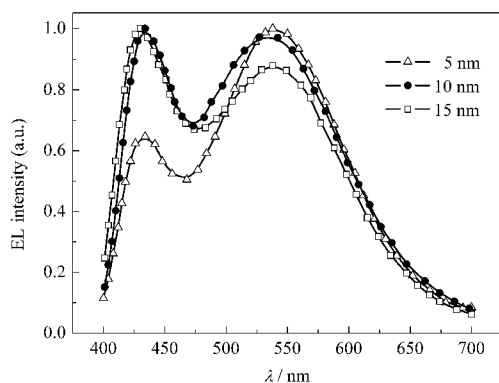
Fig.6   EL spectra of device C with various HKEthFLYPh film thickness at 9 V

tial function with the bias voltage, in accordance with the typical diode characteristic. At a forward bias of 15 V, a maximum of 8523 cd·m^{-2} with a current density of 753 mA·cm^{-2} was obtained. The turn-on voltage (defined as the bias required attaining a measurable luminance of 1 cd·m^{-2}) is 3.5 V. The inset of Fig.5 shows that the maximum power efficiency of 1.0 lm·W^{-1} was achieved at 5.5 V. Table 1 shows the EL characteristics of devices A, B, and C, such as turn-on voltage, maximum luminance, and maximum power efficiency.

In order to obtain more information about the impact of film thickness of HKEthFLYPh on the characteristics of device C, three devices with different film thicknesses of HKEthFLYPh (5, 10, and 15 nm) were fabricated with identical structure as device C shown in Fig.1. The normalized EL spectra of those devices at 9 V are shown in Fig.6. It can be seen that with the enhancement of HKEthFLYPh film thickness ranging from 5 to 15 nm, emission from NPB increases compared to that of Alq$_3$. It is due to more excitons captured and recombined in the thicker HKEthFLYPh layer, as a result, energy transfer from HKEthFLYPh to NPB increases.

3   Conclusions

In summary, we have fabricated a high performance white OLED with easy processing structure using a novel star-shaped hexafluorenylbenzene. The device with a structure of ITO/NPB (40 nm)/HKEthFLYPh (10 nm)/Alq$_3$ (50 nm)/Mg:Ag (200 nm)

was processed by thermal evaporation. The EL spectrum of the OLED shows two peaks located at 435 and 530 nm, respectively, which is almost independent on driving voltage. A maximum luminance of 8523 cd·m^{-2} at 15 V and a power efficiency of 1.0 lm·W^{-1} at 5.5 V were achieved. With increasing the film thickness of HKEthFLYPh, light emission intensity from NPB increased compared to that of Alq$_3$.

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