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High Efficiency White Fluorescent Organic Light-Emitting Diodes with HAT-CN Hole Injection Layer

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Abstract: This paper investigated a high efficiency stacked white fluorescent organic light-emitting diodes consisting of separate blue and yellow elements with a 1,4,5,8,9,11-hexaazatriphenylene-hexacar bonitril (HAT-CN) hole injection layer. The configurations of the devices are ITO/2-TNATA or HAT-CN(x nm)/NPB (25 nm)/ADN (30 nm):TBPE (2%):DCJTB(1%)/Alq₃ (20 nm)/LiF (1 nm)/Al (100 nm). According to the experimental result, the effect of HAT-CN film on carrier injection and color purity were significant. This work obtained a higher efficiency and color purity for the WOLED with HAT-CN layer, as compared to the conventional devices with copper phthalocyanine (CuPc) or 2-TNATA materials as a hole injection layer. It shows pure-white light emitting with 1931 CIE chromaticity coordinates $x=0.330\ 9$, $y=0.347\ 2$, and a current efficiency of 6.4 cd/A.

Key words: HAT-CN; WOLED; electrical properties; optical properties

HAT-CN 作为空穴注入层的高效白色 荧光有机电致发光二极管

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摘 要: 制作了 HAT-CN 作为空穴注入层的蓝、黄二基色分离的堆叠式高效有机发光二极管,器件结构为: ITO/2-TNATA 或 HAT-CN(x nm)/NPB (25 nm)/ADN (30 nm):TBPE (2%):DCJTB (1%)/Alq₃ (20 nm)/LiF (1 nm)/Al (100 nm)。实验结果表明,HAT-CN 对载流子的注入和色纯度的影响很明显。相比于传统器件将 CuPc 和 2-TNATA 作为空穴注入层,HAT-CN 作为空穴注入层得到了更高的效率和色纯度,CIE 色坐标 $x=0.330\ 9$, $y=0.347\ 2$,电流效率达到 6.4 cd/A。

关 键 词: HAT-CN; 白色有机电致发光器件; 电学特性; 光学特性

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1 Introduction

The development of efficient white organic light-emitting diodes (WOLEDs) for general lighting purposes has been intensively pursued over the last few years^[1]. Devices based on phosphorescent guest molecules are characterized not only by high efficiencies but also by high operational voltages due to the need of dispersing the phosphorescent molecules in a high energy gap matrix^[2-4]. At present, many methods are applied to improving the characteristics of WOLEDs. Several approaches have been attempted to realize this goal including the fabrication of devices with dual emitting layers^[5], stacked architectures^[6-7] and so on. A stacked architecture using CuPc material as a hole injection layer had been researched formerly. It reached a current efficiency of 6 cd/A^[8].

In our work, a new material 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitril (HAT-CN) was used as a hole injection layer in the stacked white organic light-emitting diodes consisting of separate blue and yellow elements device instead of 4, 4', 4''-tris[2-naphthyl(phenyl)amino]triphenylamine(2-TNATA). We had mainly investigated the effects of HAT-CN film on electrical and optical properties of the WOLED devices. The device using HAT-CN as a hole injection layer shows a greatly improved current efficiency and color purity.

2 Experiment

These devices were constructed as follows: ITO/2-TNATA or HAT-CN (x nm)/NPB (25 nm)/ADN (30 nm): TBPE (2%) : DCJTb (1%)/Alq₃ (20 nm)/LiF (1nm)/Al (100 nm). In the configuration, 4, 4', 4''-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA) or 1, 4, 5, 8, 9, 11-hexaazatriphenylene-hexacarbonitril (HAT-CN) is utilized as a hole injection layer (HIL), and N, N'-di(naphthalene-1-yl)-N, N'-dipheyl-benzidine (NPB) as a hole transporting layer (HTL); 9, 10-di-(2-naph-thyl)

anthracene (ADN) as the blue emitter; tris (8-Hydroxyquinoline)aluminum (Alq₃) as the electron transporting layer (ETL); green emitter, 4-(Dicyanomethylene)-2-t-butyl-6-(1, 1, 7, 7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb) and 2, 5, 8, 11-tetra-butyl-perylene (TBPe) are utilized as red and blue dyes, respectively. The molecular structures of 2-TNATA, HAT-CN, NPB and energy levels of materials used in this work are shown in Fig. 1.

The energy level values of CuPc, 2-TNATA, and HAT-CN are quoted from Ref. [8-10]. Some energy values of the materials are quoted from other paper. The HAT-CN used was purified by vacuum train sublimation in our laboratory. The devices with 2-TNATA (x nm) (Device I) or HAT-CN (x nm) (Device II) as a hole injection layer were fabricated under the same deposition conditions including deposition rates, pressure of the chamber, rolling rates of the glass plates and deposition temperature. Indium Tin Oxide (ITO) coated glass substrates were cleaned successively utilizing acetone and ethanol in an ultrasonic bath for 10 min, then were dried in a dryness ark. The surface of glass substrate was treated with air plasma before these organic materials were deposited. All the thin films were prepared by thermal evaporation in a vacuum deposition system and deposited continuously without vacuum break. Finally, organic materials including 2-TNATA or HAT-CN, NPB, ADN, DCJTb, TBPE, Alq₃ and compound cathode LiF/Al were thermally evaporated onto the plasma-treated ITO layer at a rate of 0.3 nm/s and 1 nm/s when the pressure of the chamber were 6×10^{-4} Pa. The composite film (EML) was prepared from simultaneous co-deposition of host and dopants from three separate sources.

All the devices have an emissive area of 210 mm², which is confined by a shadow mask with 14 mm×15 mm openings. The evaporation rates and thickness of the organic and metal films were monitored by four independent quartz

oscillators. The current-voltage characteristics were measured using a current/voltage unit, DC Power Supply PS-3003D. Electroluminescence (EL) characteristics and EL spectra of the devices were measured with ST-900 photometer and PMS-80. All the parameters of the devices fabricated were measured at room temperature.

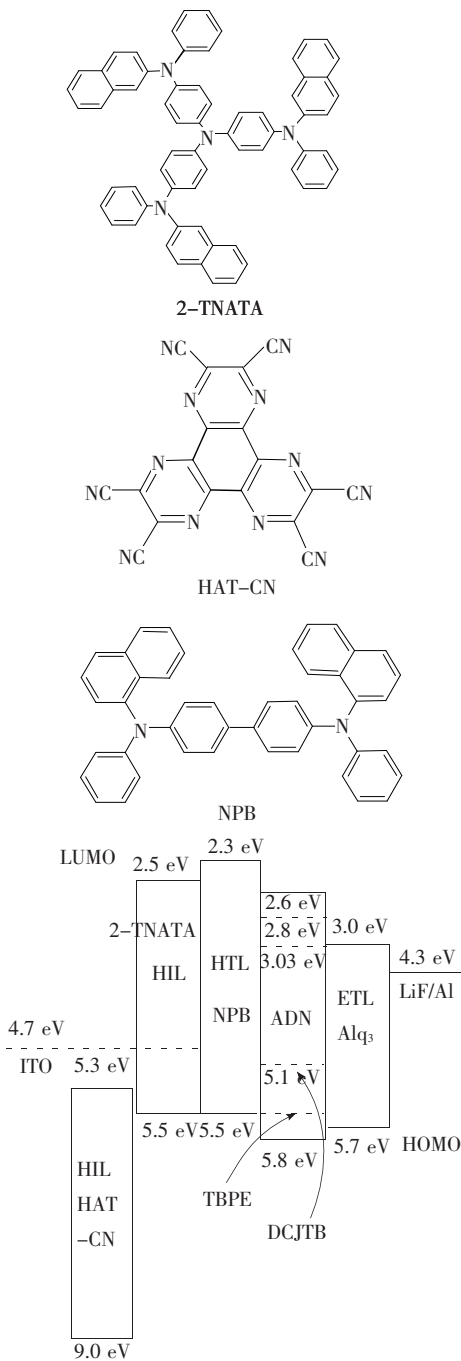


Fig. 1 Molecular structures of 2-TNATA, HAT-CN, NPB and the energy level diagram of the organic light-emitting devices.

3 Results and Discussion

Characteristics of current density J and luminance L versus voltage V for the Device I and Device II are shown in Fig. 2(a) and (b), respectively. From Fig. 2(a), it is found that current density of the devices with different thickness of HAT-CN as a hole injection layer are greatly enhanced compared with the devices of 2-TNATA at the same driving voltage. As shown in Fig. 2 (b), the initial voltage of the Device I and Device II are about 4.5 V and 3.5 V respectively. At the same voltage, the luminance of Device I is lower than that of Device II. This indicates that much more holes can be injected into the devices easily when HAT-CN film is used as a hole injection layer in devices.

The reason why the device with HAT-CN film as a hole injection is superior to the device with 2-TNATA film as a hole injection in hole injection ability is attributed to several factors. HAT-CN is a p-type organic semiconductor. In the past, HAT-CN had been used in tandem

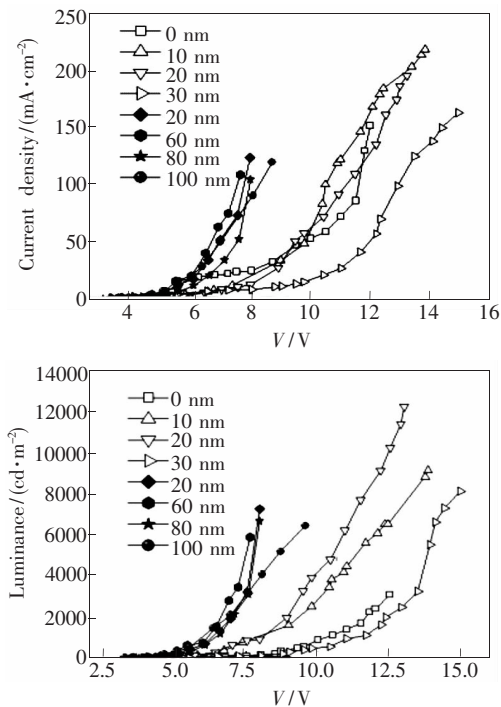


Fig. 2 (a) Current density-voltage and (b) luminance-voltage curves for Device I (hollow) and Device II (solid)

organic light-emitting diodes as intermediate connector. When an intermediate connector consists of a n-type doped layer and a p-type doped layer, the charge generation interface is formed between these two layers^[11]. Here, we used HAT-CN as a hole injection layer in the stacked white organic light-emitting diodes consisting of separate blue and yellow elements device. The charge generation interface is formed between the HAT-CN layer and the NPB layer because HAT-CN is an electron-transporting molecule that also has a strong oxidizing property^[11]. As shown in Fig. 1, it is worth noting that the 2.5 eV and 3.6 eV LUMO (Lowest Unoccupied Molecular Orbital) positions of 2-TNATA and CuPc are above the 4.7 eV Fermi level of ITO, however, the 5.3 eV LUMO position of HAT-CN is below the Fermi level of ITO. The LUMO and HOMO (Highest Occupied Molecular Orbital) positions of HAT-CN are vagarious, and both are below the Fermi level of ITO. The 0.2 eV energy barrier between the NPB HOMO and HAT-CN LUMO indicates that the electrons from NPB HOMO can be easily excited to the HAT-CN LUMO. This process is a good reason for using HAT-CN as a layer between NPB and ITO where its actual role is generating electron-hole pairs at the interface and transporting them toward the anode. In this respect, the interface between HAT-CN and ITO is not as important as copper phthalocyanine (CuPc)/indium tin oxide (ITO) interface in conventional structures such as NPB/CuPc/ITO, where the hole inject barrier between ITO and CuPc is very important^[10]. However, the experimental results show that HAT-CN can help the anode with a low work function to inject hole effectively. Therefore, supererogatory holes and electrons can be generated in the Device II.

Fig. 3 depicts current efficiency-current density curves for the Device I and Device II. We can obviously see that the current efficiency of the Device II is higher than that of Device I

with the increase of driving current density varying from 15 mA/cm² to 200 mA/cm². The device with CuPc as a hole injection layer was researched in similar configuration formerly. It reached a current efficiency of 6 cd/A. Maximum current efficiency reaches 6.4 cd/A at a current density of 30 mA/cm² without using Coumarin6 deverivative (C545) as a green dyes in Alq₃ for the Device II, and it only reaches a current efficiency of 3.5 cd/A for Device I. It can be seen that the current efficiency of the Device II with HAT-CN (80 nm) as a hole injection layer is the highest in all the devices. Effective hole transporting and the low hole-injection energy barrier are the key factors for enhancement of the current efficiency of the Device II.

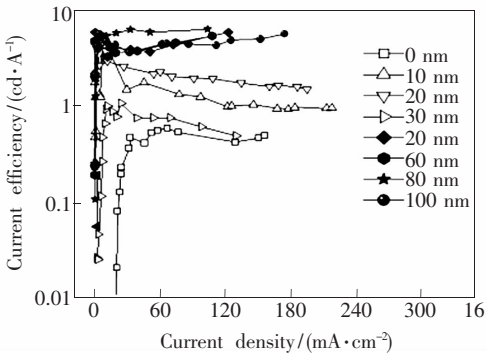


Fig. 3 Current efficiency-current density curves for Device I (hollow)and Device II (solid)

Fig. 4 shows the EL spectra characteristics of the devices with 2-TNATA (20 nm) or HAT-CN (100 nm) as a hole injection layer at different current density. In order to check which part of the emission increases quickly, the emission spectra at different current density are normalized. As can be seen, for the Device II, there is an decrease of yellow composition indicating the emission zone extended to the ADN layer with the increase of driving current density. The fluorescent characteristics emission peaks of TBPE are at 459 nm and 480 nm, and characteristics emission peak of ADN is at 460 nm^[12-13]. Emission peak of TPBE(480 nm)is enhanced with the increase of driving current density. This may be

explained as follows: the energy transfer process take place between ADN layer and Alq_3 , and the ratio of the energy transferred to the blue dye is rising with increasing current density. The Device II shows pure-white light emitting with 1931 CIE chromaticity coordinates ($x=0.330\ 9$, $y=0.347\ 2$) at a current density of $30\ \text{mA}/\text{cm}^2$, but it has relatively worse color stability than

the Device I as shown in the inset of Fig. 4. It is important to supply a stable driving current for the Device II. We can dope Coumarin6 deverivative (C545) into Alq_3 or insert a hole blocking layer between ADN and Alq_3 for further improving the EL characteristics of the Device II.

4 Conclusion

A stacked white organic light-emitting diodes with a new hole injection material HAT-CN and a conventional hole injection material 2-TNATA were constructed. Two kinds of devices have been compared. The former has been shown as a high current efficiency and color purity device with a maximum efficiency of $6.4\ \text{cd}/\text{A}$, CIE coordinates $x=0.330\ 9$, $y=0.347\ 2$ at a current density of $30\ \text{mA}/\text{cm}^2$. The former and the latter both are current dependent devices. In addition, the former has a low initial voltage.

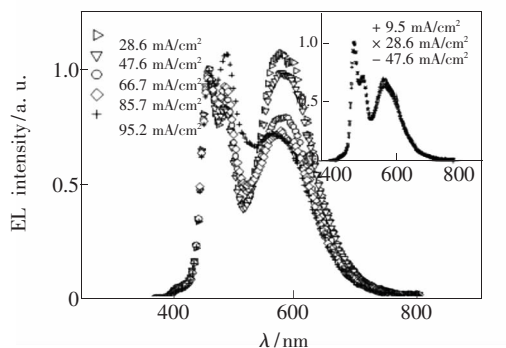


Fig. 4 EL spectra of the devices with the 20 nm thick film of 2-TNATA and the 100 nm thick film of HAT-CN at different driving current density

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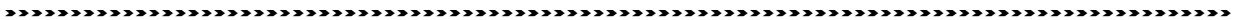
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