Organic alternating current electroluminescence device based on 4,4′-bis(N-phenyl-1-naphthylamino) biphenyl/1,4,5,8,9,11-hexaazatriphenylene charge generation unit

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ABSTRACT

An organic alternating current electroluminescence (OACEL) device based on 4,4′-bis(N-phenyl-1-naphthylamino) biphenyl (NPB)/1,4,5,8,9,11-hexaazatriphenylene (HAT-CN)/tris(8-hydroxy-quin-olinato) aluminum (Alq3) doped with cesium carbonate (Cs2CO3) internal charge generation unit is demonstrated. Maximum luminance of 299 cd/m2 is observed for Alq3 doped with 10-(2-Benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1) benzopyropyrano (6,7-8-I,j)quinolizin-11-one (C545T) fluorescent emission layer when driven with a peak–peak voltage of 80 V at 120 kHz. The key charge-generation role of NPB/HAT-CN interface is studied experimentally. Furthermore, influence of evaporation sequence of this internal charge generation unit on OACEL performance is investigated. This work demonstrated that the undoped charge generation unit – NPB/HATCN, can also be a good candidate for charge generation unit of OACEL device.

1. Introduction

Alternating current electroluminescence (AC-EL) has been widely studied in the fields of lighting and display, especially for AC-EL devices based on inorganic materials, such as sulfide phosphors [1–7]. However, there are two problems in this type of devices: (1) less choice of materials for full color demonstration and (2) the low photoluminescent quantum efficiency of inorganic phosphors [1,8]. Recently, organic AC-EL (OACEL) devices have received considerable attention for their advantages of wide selection of materials by engineering chemical structures and high quantum efficiency [5,8–11]. Unlike traditional organic EL devices which are operated by direct current (DC), OACEL devices are operated under AC condition. Thus, extra power losses as well as cost, which are induced by additional electronic equipment for converting AC to DC, can be avoided when the device is adjusted to the city power network after further researches. Typically, OACEL devices are composed of thin organic layers placed on/below a dielectric layer or sandwiched between a pair of dielectric layers [4,12–19]. Unlike their inorganic counterparts, light emission in OACEL is achieved by recombination of holes and electrons that are generated by an internal charge generation unit (CGU). Typically, there are two types of CGUs in OACEL devices. One is inorganic nanoparticles embedded in organic layer [12,13,18], such as ITO nanoparticles [12], single- or multi-walled carbon nanotubes [13,18], and nanographite platelets [20]. The emission intensity of these devices, however, is still low,
which may be caused by the poor charge-generation ability as well as larger carrier injection barrier between those nanoparticles and organic materials. Moreover, some nanoparticles, such as carbon nanotubes [13,18], are difficult to purify, which will limit further development of device performance. Compared to inorganic nanoparticles embedded in organic layer, another type is P (or N) type electrical doping layer [10,14–16,19], such as P-type poly (N,N-bis-(4-butylphenyl)-N,N-bis(phenyl)benzidine) (Poly-TPD) layer doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) [10], P-type N,N-tetrakis (4-methoxyphenyl)-benzidine (MeO-TPD) layer doped with F4TCNQ, as well as N-type 4,7-dipheny-1,10-phenanthroline (Bphen) layer doped with cesium [14]. The performance has been improved for devices based on these electrical doping CGUs. However, sophisticated doping technology still obstacles its wide application.

The 4,4′-bis(N-phenyl-1-naphthylamino) biphenyl (NPB) and 1,4,5,8,9,11-hexazatriphenylene-hexacarbonitrile (HAT-CN) interface serving as an effective CGU has been demonstrated in many tandem DC organic light emitting diodes. It is shown that using NPB/HAT-CN CGU can improve the current efficiency as well as power efficiency of tandem OLEDs compared with their single control OLEDs, indicating that the NPB/HAT-CN CGU has excellent charge generation ability as well as outstanding carrier injection ability. Furthermore, the fabrication of NPB/HAT-CN CGU is based on layer by layer deposition technology, which will reduce the cost compared to doping ones. In this study, the application of NPB/HAT-CN CGU in OACEL device is demonstrated. A tris(8-hydroxy-quinolinato) aluminum (Alq3) layer doped with a fluorescent dye of 10-(2-Benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1)benzopyropyran(6,7-8-lj) quinolizin-11-one (C545T) is used as the emission layer. The maximum luminance of 299 cd/m² is achieved when the OACEL device is driven with a peak–peak voltage of 80 V at 120 kHz.

2. Experimental details

In this study, 100 nm thick indium tin oxide (ITO) coated glass with a sheet resistance of 25 Ω/cm was used as substrate. Prior to device fabrication, ITO substrate was cleaned with deionized water and acetone, and then was exposed to an UV-ozone ambient for 1 min. Silicon dioxide (SiO2) dielectric layer was used to prevent charge injection from the bottom and top electrodes, as well as to store the charges generated from the internal CGU. The SiO2 layers were deposited by radio frequency (RF) magnetron sputtering in a high purity argon atmosphere at a pressure of 1 Pa. A sputtering rate of 0.02 nm/s was achieved by an RF power of 200 W for the first insulating layer, and the RF power for the second insulating layer located on top of the organic material was reduced to about 150 W to prevent sputter-induced damage [14,16].

An AC sinusoidal driving voltage was achieved by an arbitrary function generator (RIGOL DG1022) connected to a bipolar linear power amplifier. Current was monitored by a digit multimeter (Keithley 2110). Luminance was recorded by a calibrated silicon photodiode. Photoluminescence and Electroluminescence spectrum were recorded by fluorescence spectrophotometer (FluoroMax-4, HORIBA Jobin Yvon Inc.) and PR650 spectrometer (PHOTO RESEARCH Inc.) respectively. Time resolved voltage and light emission signal (converted by a photodiode) were monitored by a Tektronix TDS2024B oscilloscope. The direct current and voltage were supplied and detected by a computer controlled sourcemeter (Keithley 2602). All above measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

As shown in Fig. 1(a), Device A with structure of ITO/SiO2 (50 nm)/NPB (20 nm)/HAT-CN (20 nm)/Alq3:Cs2CO3 (10 nm, 20 vol%)/Alq3 (40 nm)/Alq3:C545T (20 nm, 2 vol%)/NPB (60 nm)/HAT-CN (20 nm)/Alq3:Cs2CO3 (10 nm, 20 vol%)/SiO2 (50 nm)/Al (100 nm) was fabricated to study the performance of OACEL. The luminance–frequency performance of Device A is shown in Fig. 1(b). A parabola-shaped curve is exhibited with the frequency increase. At the optimal frequency of 120 kHz, the voltage–luminance characteristic of Device A is shown in Fig. 1(c). The maximum luminance reaches 299 cd/m² at peak–peak voltage of 80 V and the threshold voltage is as low as 45 V. In Fig. 1(d), the AC current density increases with the increase of voltage and stays above 1 × 10⁶ A/m². The I–V curve shows an approximately linear relationship between alternating current and voltage. However, in the DC I–V test, just as shown in the insert of Fig. 1(d), the current density is lower than 2 × 10⁻³ A/m² because of the dielectric characteristic of SiO2 layer, and no light emission can be observed. Thus, the contribution of leakage current on the AC emission can be neglected.

To understand the influence of frequency on the device performance, time resolved electroluminescence of Device A at different frequencies is studied. Fig. 2 depicts the time-varying photodiode traces under same driving voltage but different frequencies. Apparently, with the frequency increases, the peak value of light emission pulses in a cycle decreases evidently and the number of light emission pulses in a certain time variation increases. Determined by both emission strength and number of pulses, the luminance in a certain period of time (t₀ ~ t₁), referred as L, can be calculated as Eq. (1).

\[ L = (t_1 - t_0) \cdot f \cdot \int_{t_0}^{t_1} pdt \]  

(1)

where \( P \) is the strength of the emission pulse, \( f \) is the frequency. A parabola shape of luminance–frequency curve shown in Fig. 1(b) may be caused by the following factors: on one hand, limited by mobility, fewer charge carriers move into the EML in one AC voltage cycle as the frequency gets higher. So the emission strength reduces and the integration decreases as well. On the other hand, however, the
increase of frequency means more cycles in the time variation and more emission pulses are integrated. Thus, affected by both factors, the luminance–frequency curve shows a parabola shape.

Typically, there are two different mechanisms to explain the EL emission of OACEL. One believes that the EL emission derive from the regular recombination of excitons [14,20]. Another is that the EL emission comes from direct interband transitions under high internal electric field, and the EL peak will blue shift compared with that of the regular excitons recombination [21,22]. To understand EL mechanism of Device A, the electroluminescence spectra is recorded. In Fig. 3, the EL spectrum peak of the OACEL (518 nm) is very close to the PL spectrum of C545T (512 nm) and these two spectra match very well, which confirms that the EL emission of Device A comes from the recombination of Alq3 single excitons. A very weak emission peak is observed at about 610 nm, which may result from the optical microcavity effect of Device A.

To understand the role of HAT-CN/NPB structure in OACEL device, two devices with structures of ITO/SiO2 (50 nm)/HAT-CN(20 nm)/Alq3:Cs2CO3(40 nm)/Alq3:Cs545T(20 nm, 2 vol%)/NPB(60 nm)/HAT-CN (20 nm)/SiO2 (50 nm)/Al(100 nm) (Device B) and ITO/SiO2 (50 nm)/NPB (20 nm)/HAT-CN (20 nm)/Alq3:Cs2CO3(10 nm, 20 vol%)/Alq3:Cs545T(40 nm)/Alq3:Cs2CO3(20 nm, 2 vol%)/NPB(60 nm)/HAT-CN (20 nm)/SiO2 (50 nm)/Al(100 nm) (Device C) are fabricated (seen in Fig. 4(a)). Compared with Device C, a 20-nm thick NPB layer close to the ITO electrode side is omitted in Device B, which makes Device B containing only one NPB/HAT-CN structure. The luminance–voltage characteristics of Devices B and C at 50 kHz are shown in Fig. 4(b). Obviously, Device C with two CGUs on each side of the EML performs better in luminance which reaches 114 cd/m², and the threshold voltage is about 60 V. However, no light emission can be detected for Device B with the driving voltage increase. In addition, compared with Device A, Alq3:Cs2CO3 layer with a thickness of 10 nm omits in both Devices B and C. Thus, the luminance–voltage characteristics of Devices B and C also demonstrate that the Alq3:Cs2CO3 layer is not crucial for charge generation.

The CGU of NPB/HAT-CN/Alq3:Cs2CO3 structure plays an important role for the performance of OACEL. To further
understand the charge transport mechanism of the NPB/HAT-CN/Alq3:Cs2CO3 CGU under AC condition, Device D with structure of ITO/NPB(40 nm)/HAT-CN(20 nm)/Alq3:Cs2CO3(40 nm, 20 vol%)/Al(100 nm) was fabricated. Besides, a control device with structure of ITO/NPB(60 nm)/Alq3:Cs2CO3(40 nm, 20 vol%)/Al(100 nm) (Device E). Just as shown in Fig. 5(a). All of those two devices were tested by sweeping the DC voltage from −15 V to 15 V. Here the ITO electrode is used as anode, and Al electrode is used as cathode. The current density–voltage characteristics of Devices D and E are shown in Fig. 5(b). In the control Device E, the hole injection barrier of ITO/NPB interface and the electron injection barrier of Alq3:Cs2CO3/Al interface is low when the device works in the positive bias region. When the Device E works in the negative region, the hole injection interface changes to the Alq3:Cs2CO3/Al interface, and the electron injection interface changes to the ITO/NPB interface. Because of the significant electron blocking property of NPB layer [23] and the hole blocking property of Alq3:Cs2CO3 layer [24], charge injection of Device E in the negative region are suppressed. Thus, a typical rectification I–V curve of the control Device E is shown in Fig. 5(b). For Device E, however, a bipolar transport property is exhibited in Fig. 5(b). In the negative bias region, although external charge injection was strongly suppressed, Device D still exhibits high conductance because of the strong charge generation property of NPB/HAT-CN/Alq3:Cs2CO3 structure. In the positive bias region, external charge can be injected into the organic semiconductor layer easily, thus the Device D is still in the conductance state. However, extra energy is needed to overcome the transport barrier in NPB/HAT-CN interface, which is induced by the charge transfer from the highest occupied molecular orbit of NPB to the lowest unoccupied molecular orbit of HAT-CN [25]. Thus, in the positive bias region, higher driven voltage is needed for Device D than Device E at the same current density.

**Fig. 2.** Time-varying photodiode traces under same driving voltage at 1 kHz, 2 kHz, 4 kHz and 10 kHz. With the increasing of the frequency, the emission value in single cycle decreases evidently but the emission quantity gets large simultaneously.

**Fig. 3.** EL spectrum of the Device A at 50 V, 120 KHz. The photoluminescence spectrum of C545T is shown as reference.
Considering the charge generation process of NPB/HAT-CN CGU, light emission process of Device A can be understood as follow: when the negative half cycle of the sinusoidal signal is applied on Device A, just as shown in Fig. 6(a), the electrons generated by CGU close to ITO electrode and holes generated by CGU close to Al electrode move towards each other driven by external electric field, and form excitons in Alq3:C545T layer for emission. At the same time, the holes and electrons move to insulating layers close to ITO and Al electrodes respectively, and accumulate at the interface of insulator and organic layer. Sequentially, when the positive cycle arrives, the electric field direction within the device reverses under the applied voltage (shown in Fig. 6(b)). Driven by the electric field, holes stored at the interface of insulator close to ITO electrode move and accumulate at NPB/HAT-CN interface, while electrons stored at the interface of insulator close to Al electrode accumulate at another NPB/HAT-CN interface. With the increase of electric field, zener tunneling across the HOMO–LUMO gap will occur [26]. Electrons in NPB HOMO tunnel into Alq3 and leave behind holes. Thus, electrons are transported towards the ITO electrode and then recombine with the holes accumulated in NPB. Also, the holes left behind in the NPB are recombined with the electrons accumulated in HAT-CN. Then, the system gets back to the original situation and be ready for the next cycle. However, in Device B, there is only one effective CGU, the adjacent NPB/HAT-CN layers. In negative cycle, there are not enough electrons for charge recombination with the holes separated by the CGU. So it gives a very lousy luminance.

In addition, influence of process sequence on the performance of OACEL is also studied in this work. Device F with inverted structure of ITO/SiO2(50 nm)/Alq3:Cs2CO3(10 nm)/HAT-CN(20 nm)/NPB(60 nm)/Alq3:C545T(20 nm)/Alq3(40 nm)/Alq3:Cs2CO3(10 nm)/HAT-CN(20)/NPB(20 nm)/SiO2(50 nm)/Al(100 nm) (seen in Fig. 7(a)). The time-varying luminance signal of Devices A and F are shown in Fig. 7(b). Obviously, in Device A, the light is emitted in the negative voltage cycle and the device condition recovers in the positive cycle. Oppositely, the light emission of
Device F is in the positive voltage cycle. The luminance–voltage characteristics of Devices A and F are shown in Fig. 8. Interestingly, Device F with inverted structure exhibits poor luminance performance. A possible reason is that the sequence of NPB and HAT-CN influences the hole injection efficiency of the CGU. As reported by Cephas et al. [27], CGU with NPB/HAT-CN structure, which is used in Device A, exhibits almost 100% hole injection efficiency, much higher than the CGU with HATCN/NPB used in Device F.

4. Conclusions

In conclusion, a new AC driven organic light-emitting device which has undoped internal CGUs to provide the charge carriers instead of injecting from the electrodes was demonstrated. The use of NPB and HAT-CN as CGU is proved to perform excellently and a remarkable fluorescent luminance is observed. The particularly parabola-shaped curve of the luminance–frequency characteristic caused by the limitation of the mobility of charge carriers is theoretically and experimentally explained with the help of time resolved measurements. In addition, the luminous properties of an invert-structured device and the influence of the process sequence of NPB and HAT-CN are discussed.

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