

# Highly efficient organic light-emitting devices beyond theoretical prediction under high current density

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**Abstract:** We develop a simple method to improve external quantum efficiencies (EQEs) of OLEDs under a wide range of current density. An insulating inorganic ultrathin layer (LiF) was sandwiched between exciton formation layer and electron transporting layer. A maximal EQE of 5.9% in a DCM based fluorescent OLED, which far exceeds the theoretical upper limit of 3.7%, was obtained under the current density of 487 mA/cm<sup>2</sup> with a brightness maximum of 76740 cd/m<sup>2</sup>. The similar electroluminescence properties were also obtained in a C545T based green OLED using this method. The overall enhancement of EQE, and the nonlinear enhancement of EQE at high current density in these devices are attributed to the effect of electrical field on excitons.

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**OCIS codes:** (160.4890) Organic materials; (230.3670) Light emitting diodes.

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## 1. Introduction

Organic light-emitting devices (OLEDs) are attracting much attention for their potential applications in back light unit of flat panel displays, full color displays and solid state lighting [1–3]. Recently, OLEDs have reached a preferable performance with regard to efficiency, brightness and stability [4,5]. However, most reported OLEDs showed high efficiency under the current density less than 100 mA/cm<sup>2</sup>, because the nonradiative losses become more serious as injection current density increases [4–6], resulting in an undesirable efficiency roll-off problem. This problem imposes challenges on OLED applications as well as developing of electrically pumped organic laser devices (OLDs) [7].

Due to their appealing advantages, especially with respect to tunable emission in wide range, laser sources based on low-cost organic semiconductors are considered as an attractive alternative to their inorganic counterparts [7–9]. In principle, as has been done for inorganic diodes, to realize an electrically pumped laser, it is necessary to drive a LED structure with optical feedback at an excitation density higher than lasing threshold. One of the main difficulties is the rather high excitation density required in these geometries which was estimated from the performance of reported OLEDs and the optical pumped experiments [9]. A high efficiency OLED working at higher driving current densities is much needed towards lowering the threshold and enhancing the output power. That means some of the exciton quenching processes, which was widely observed in OLEDs, due to singlet-singlet annihilation, singlet–polaron annihilation, and optical absorptions by polarons, singlet excitons, triplet excitons and metal electrodes must be controlled [10,11].

A few OLEDs with p-i-n or tandem structure presented reduced efficiency roll-off [12,13], while their fabrication processes are complicated, and appropriate n-doping materials for p-i-n OLEDs or interlayer connecting units (ICU) materials for tandem OLEDs are still in lacking. Hence, there is a need for a simple and effective method of achieving high performance OLEDs under high current density.

In this paper, we report a simple method to obtain extraordinarily high external quantum efficiencies (EQE). We will show that greatly improved performance of small molecular based OLEDs comes only from adding a layer in their normal structures. A thin film of LiF was inserted between a fluorescent doped emitting layer (EML) and an electron transporting layer (ETL) for the 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) based red OLED and the 10-(2-Benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1)benzopyrroprano(6,7-8-I,j) quinolizin-11-one (C545T) based green OLED, respectively. An EQE of 5.9% is obtained for the red OLED, which is much higher than the theoretical upper limit of 3.7% [14–16]. In this respect, the obtained EQE of 4.38% for the green one is similar in exceeding the theoretical upper limit of 4.0%. Compared with those of normal structures, the EQE at the highest current density is increased 3.6-fold for the red OLED, and 2.6-fold for the green OLED, respectively. Moreover, both OLEDs show an increased EQE after a certain current density. The factors affecting the efficiency of OLEDs were analyzed. The transcendental value beyond the classical limit is attributed to the

change of singlet and triplet exciton formation ratio resulting from electrical field effect on the excitons.

## 2. Experiments

Four samples were fabricated with the following structure.

Sample A: Glass/ITO/MoO<sub>3</sub> (1 nm) /NPB (74 nm) /Alq<sub>3</sub>:DCM (33 nm)/ LiF (0.3 nm) /Alq<sub>3</sub> (45nm)/LiF (1 nm)/Al.

Sample B: Glass/ITO/MoO<sub>3</sub> (1 nm) /NPB (74 nm) /Alq<sub>3</sub>:DCM (33 nm) /Alq<sub>3</sub> (45nm)/LiF (1 nm)/Al.

Sample C: Glass/ITO/MoO<sub>3</sub> (1 nm) /NPB (74 nm) /Alq<sub>3</sub>: C545T (33 nm)/ LiF (0.3 nm) /Alq<sub>3</sub> (45nm)/LiF (1 nm)/Al.

Sample D: Glass/ITO/MoO<sub>3</sub> (1 nm) /NPB (74 nm) /Alq<sub>3</sub>: C545T (33 nm) /Alq<sub>3</sub>(45nm)/LiF (1 nm)/Al.

For all examples, all layers were deposited by high-vacuum ( $5 \times 10^{-4}$  Pa) thermal evaporation method. To improve hole injection and interface stability [17], Molybdenum oxide (MoO<sub>3</sub>) was used as a buffer layer that deposited onto transparent and conductive indium tin oxide (ITO) anode. A 74nm-thick layer of N, N-bis(3-naphthalen-2-yl)-N, N-bis(phenyl)benzidine (NPB) is used to transport holes to the EML consisting of laser dye (1 wt %, DCM or C545T) doped in tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) (33nm). Then a thin layer of LiF (0.3nm) was inserted between the EML and the ETL Alq<sub>3</sub> (45nm). The cathode composes of 1 nm LiF capped with 100 nm Al. The evaporation rates were monitored *in situ* by quartz crystal oscillator. Sample A and C are DCM based red OLED and C545T based green OLED, respectively. Sample B and D were fabricated as a referenced OLED without LiF interlayer for comparison. Electroluminescence (EL) spectra, Current-voltage-brightness characteristics were measured by a Photo Research PR-705 SpectraScan System driven with a Keithley 2400 source meter. The EQE values were obtained based on luminance, EL spectra, current densities, and the eye-sensitivity function [18]. Film thicknesses were measured with an Ambios XP-1surface profiler. Fluorescent quantum yield ( $\Phi_f$ ) of fluorescent material was measured with an Avantes fiber optic spectrometer system through relative measurement with a solution of quinine bisulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> ( $\Phi_f=0.515$ ) as standard [19]. All measurements were conducted in air at room temperature.

## 3. Results and discussion

Figure 1 shows the structure of sample A with energy level diagram. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) values are extracted from the references [15, 17].

The luminance and EQE as a function of current density (J) for sample A and B are shown in Fig. 2(a). From the photoluminescence (PL) quantum efficiency (74%) of a DCM:Alq<sub>3</sub> film [14], the theoretical upper limit of EQE for DCM based OLED was approximate 3.7%. It shows that sample B has an average EQE of 2%, and exhibits an efficiency roll-off characteristic. While sample A shows an average EQE of 4.5%, clearly exceeding the theoretical upper limit of 3.7%. As shown in Fig. 2(b), sample A has a EL peak at around 586 nm. The maximal EQE of 5.9% is obtained at the current density maximum of 487 mA/cm<sup>2</sup>, corresponding to a maximum luminance of 76740 cd/m<sup>2</sup>. The EQE at the highest current density and the maximal luminance of sample A are 3.6 times and 3.2 times higher than that of sample B, respectively. It suggests that nonradiative losses in OLED are especially severe under high driven current densities such as singlet-singlet and singlet-heat annihilations (SSA and SHA) [20]. Therefore, most OLEDs reach a maximal efficiency under a low driven current density about 100 mA/cm<sup>2</sup>, corresponding to a luminance of several hundred cd/cm<sup>2</sup>. In this respect, the minor change in the structure of sample A leads to an evidently advance in the EL properties under higher current density.

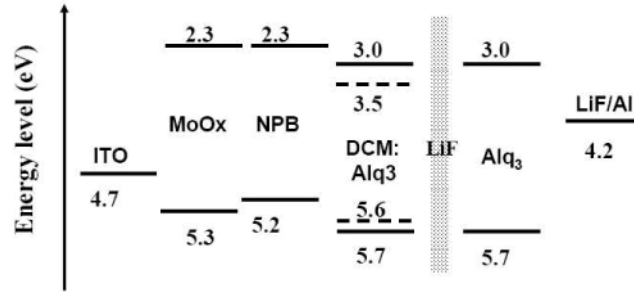


Fig. 1. The energy level diagram of the sample A

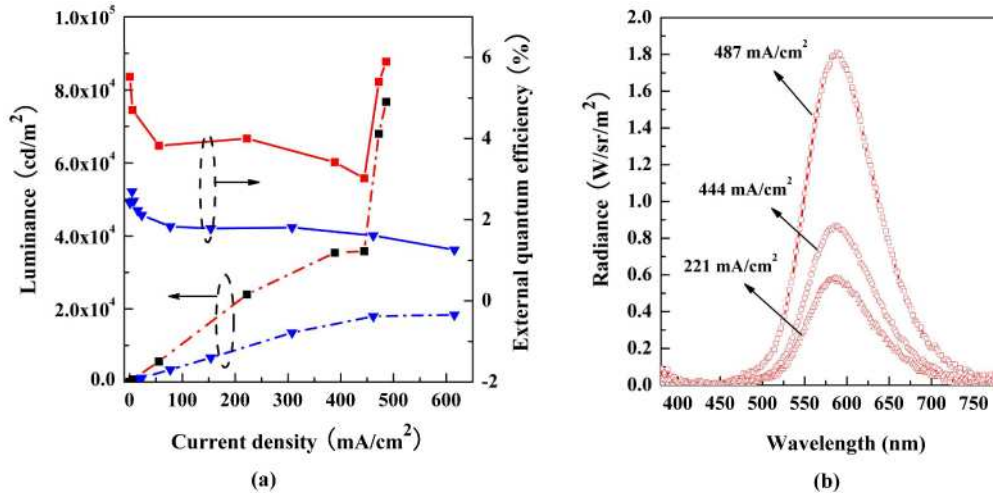


Fig. 2. (a) Luminance and EQE vs current density of sample A (red curve) and B (blue curve). (b) EL spectra of sample A under different current density.

Improvement in EQE was also observed in C545T based green OLEDs (sample C). As shown in Fig. 3(a), sample D shows an average EQE of 1.4%, and an efficiency roll-off characteristic. However, the EQE ~J curve of sample C is similar to sample A under higher current density. The EQE of sample C has an average value of 3.57%. It shows a maximal value of 4.38% at 300 mA/cm<sup>2</sup>, and an efficiency roll-off among 300 ~750 mA/cm<sup>2</sup>, and then an efficiency increasing among 750~900 mA/cm<sup>2</sup>. The measured fluorescent quantum efficiency of C545T is about 0.8. Then the theoretical upper limit of EQE can be estimated to be about 4.0% for the C545T based green OLEDs. The EL spectra of sample C expressed in spectral radiance are shown in Fig. 3(b). It shows that the emissive peak and full width at half maximum (FWHM) of sample C is steady under different current densities.

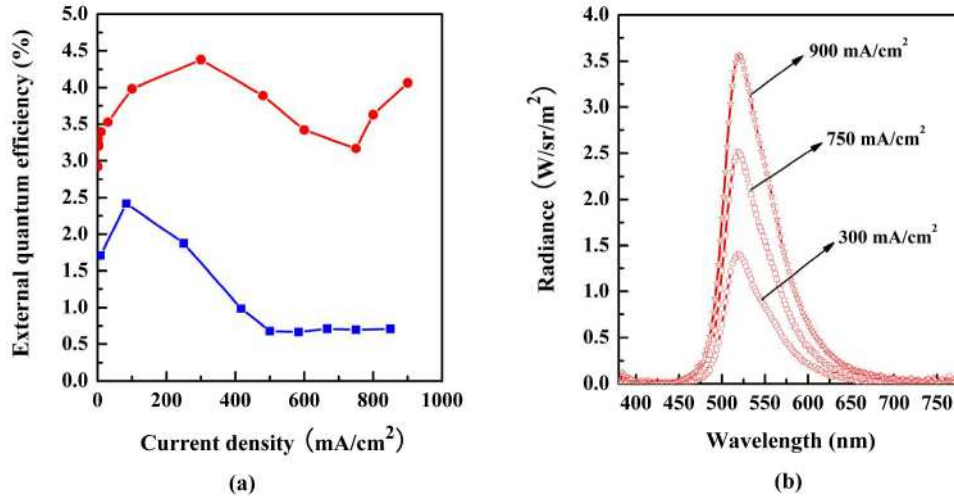


Fig. 3. (a) External quantum efficiency as a function of current density for sample C (red) and D (blue). (b) EL spectra of sample C under different current density.

Figure 4 compares the I-V characteristics and EL spectra between sample A and B. In both OLEDs, light emission is from the guest fluorescent molecule DCM. It shows that the I-V characteristics and EL spectra of sample A and B are similar in curve shape. The EL spectra of both samples are unchanged when driving at different current density. Such comparisons are also obtained for the C545T based OLEDs, and give the similar results.

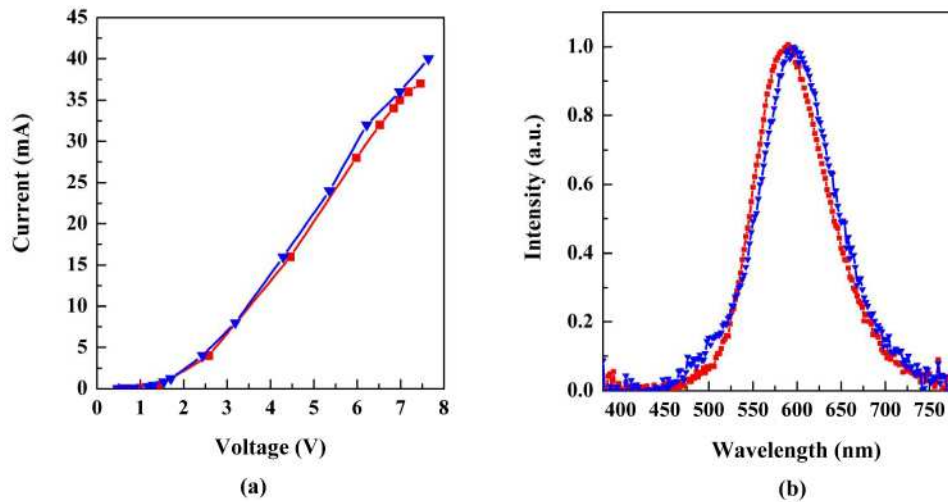


Fig. 4. Current-voltage characteristics (a) and EL spectra (b) of sample A (red) and sample B (blue).

It is well known that external quantum efficiency ( $\eta_{ext}$ ) of an OLED can be described as follows:

$$\eta_{ext} = \eta_r \phi_f \chi \eta_{ph} \quad (1)$$

where  $\Phi_f$  is the intrinsic fluorescent quantum efficiency that governed by the emitting material, such as DCM in sample A and B.  $\eta_{ph}$  is the light out-coupling efficiency, which is often assumed to be about 20% as estimated from  $\eta_{ph} = 1/2n^2$  ( $n$  is the refractive index of the emitting material) inherent for a glass substrate OLED;  $\chi$  is the ratio of singlet excitons to

total excitons, which is 25% for the fluorescent molecular dyes according to the spin dependent.  $\eta_{\gamma}$  is the balance factor of injected electron-hole. According to the tested EL and I-V properties, it can be inferred that the enhancement of EQE in sample A or sample C is not due to the change of parameters  $\Phi_f$ ,  $\eta_{ph}$ , and  $\eta_{\gamma}$ . Since the EQE of sample A at the highest current density is improved by a factor of 3.6 compared to the reference sample B, the corresponding  $\chi$  in sample A should be as high as 40%. Traditionally, it is interpreted that the yield of electrically-generated singlet and triplet exciton formation ratio ( $\gamma_{s/t}$ ) in organic molecular semiconductors is 1:3, and then  $\chi$  is limited to 25%. In spite of this, there still many studies bear out the supposition that one can manage the singlet and triplet excitons for efficient fluorescent OLEDs [15]. In this study, the reason for a higher  $\chi$  in sample A and C is not clear. One possible reason might be the 1:3 formation rates of intermediate charge-transfer (CT) states changing a lot by inserting LiF thin layer between the doping EML and the ETL, which leads to an enlarged singlet exciton fraction and a higher  $\chi$ .

Furthermore, by inserting the LiF layer, the luminance and EQE of sample A and C increase nonlinear at high current density. We attribute this to the field effect on excitons [21]. In order to build a framework for analyzing the effect of internal electrical field on the radiative emission properties in molecular OLED, it's helpful to re-examined the analysis of excitons in polymer light-emitting diodes (PLEDs). Recently, both experimental and theoretical evidence indicates that the  $\gamma_{s/t}$  in conjugated polymers can exceed the 1:3 spin statistics due to the effect of the electric field. It has been shown that the ratio  $\gamma_{s/t}$  increases smoothly with the electrical field in p-phenylene-vinylene oligomer based PLED [20]. However, there exists a threshold electrical field. When the field strength is larger than the threshold, the  $\gamma_{s/t}$  increases rapidly with the field strength.

It can be assumed that there are the similar field effects in molecular OLEDs. But the key obstacle is that, with the increasing of electrical field strength, on the one hand, the  $\gamma_{s/t}$  increases, the efficiency should be raised; on the other hand, the nonradiative losses which dependent on the field strength (like the SSA and SHA) grow up simultaneously, the efficiency should be come down. The two processes compete against each other. According to the previous theoretical calculation on the position of recombination zone [22], the inserted ultra-thin layer of LiF is adjacent to the exciton recombination zone. From the similar I-V characteristics of sample A and B, we assume that the ultra-thin layer of insulated LiF brings little shift in the average electrical field strength of the two devices under the same current density, but the local electrical field strength in the exciton region may be changed substantially. The enhancement of EQE of sample A and C under high current density in Fig. 2 and Fig. 3 illustrates a clear threshold, above which the EQE increases more rapidly. The electrical field strength inside exciton formation area should be appropriate, which must be higher than a threshold that leading to an increase of  $\gamma_{s/t}$ , and be lower than the value that can induce exciton dissociation. The detailed improvement mechanism investigation is underway.

#### 4. Conclusions

In summary, we demonstrated that EQE of fluorescent OLEDs can be enhanced significantly over a wide range of current density simply by using a thin interlayer of LiF inserted between the EML and the ETL. Simultaneously, EQE that exceeds theoretical upper limits has been observed at the highest injection current density. We attribute this kind of EL performance to an electrical field effect on excitons.

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