

High efficiency yellow fluorescent organic light emitting diodes based on m-MTDATA/BPhen exciplex

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Abstract High efficient yellow organic light emitting diodes (OLEDs) based on exciplex were reported. The exciplex was formed by 4, 4', 4''-tris [3-methylphenyl (phenyl) amino]-triphenylamine (m-MTDATA) and 4, 7-diphenyl-1, 10-phenanthroline (BPhen). The resulting yellow OLEDs exhibited an external quantum efficiency of over 7%, which is attributed to the effective energy back transfer from exciplex triplet state to exciplex singlet state. The maximum power efficiency of 25 lm/W was achieved. Doping a yellow phosphor Ir(bt)₂(acac) into m-MTDATA: BPhen blend, a high efficiency device was achieved with a turn-on voltage of 2.1 V, maximum power efficiency and external quantum efficiency of 86.1 lm/W and 20.7%, respectively.

Keywords organic light-emitting diodes (OLEDs), fluorescent, exciplex

1 Introduction

Organic light emitting diodes (OLEDs) are now gradually commercialized through the ceaseless study by researchers from both colleges and companies for the merits of high efficiency and great potential in the applications of display and solid-state lighting [1–3]. To enhance the electroluminescence efficiency of OLEDs, a variety of emission materials based on fluorescence and phosphorescence have been presented [4,5]. For OLEDs using fluorescence materials, the internal quantum efficiency (η_{int}) is usually not higher than 25% by the limitation of spin-forbidden. In general, the external quantum efficiency (EQE) of fluorescence devices depends on four factors:

$$EQE = \eta_{\text{out}} \times \eta_{\text{fl}} \times \eta_{\text{s}} \times \gamma, \quad (1)$$

where η_{out} is the light out coupling efficiency which is considered to be 20%, η_{fl} is the fluorescence efficiency assumed to be 1 as unity yield fluorescence emitters, η_{s} is the singlet formation ratio assumed to be 25%, and γ is the charge balance factor which can also be assumed to be 1 if the device structure and transport characteristics are adjusted in an appropriate manner. Above all, the upper limit of EQE is calculated to be 5% ($EQE \approx 0.2 \times 1 \times 1 \times 0.25 = 0.05$). Considering the large proportion of triplets (75%) in electrical excited excitons, the triplet-triplet annihilation (TTA) in fluorescent OLEDs is inevitable and will generate one singlet from two triplets. So, for the TTA-involved process of singlet generation, the modified estimation for EQE is [6]

$$EQE = \eta_{\text{out}} \times \eta_{\text{fl}} \times (\eta_{\text{s}} + \eta_{\text{t}}/2) \times \gamma, \quad (2)$$

where η_{t} is the triplet formation ratio assumed to be 75%. Then, the upper limit of EQE goes to $\sim 0.2 \times 1.0 \times (0.25 + 0.75/2) \times 1.0 \sim 12.5\%$. Then development of thermally activated delayed fluorescence (TADF) materials by Adachi's group enables energy transfer from triplet to singlet through reverse intersystem crossing (ISC) since their small singlet-triplet split, which can further improve the theoretical EQE limit of fluorescent OLEDs comparable to phosphorescent OLEDs to 20% [7,8]. Meanwhile, Adachi's group also proposed a simple strategy of two mixed materials (i.e., donor and acceptor) to realize higher efficiency than fluorescent EQE limitation of 5% by using the high reverse ISC efficiency of the intermolecular excited state (which is, exciplex state) [9,10]. If the photoluminescence (PL) efficiency of a donor-acceptor system is 100%, and all the generated triplet excitons can convert into singlet excitons, the theoretical limit is supposed to be 20%. Here we present a yellow fluorescent OLED composed of electron-donating 4, 4', 4''-tris [3-methylphenyl (phenyl) amino]-triphenylamine (m-MTDATA) and electron-accepting 4, 7-diphenyl-1,10-phenanthroline (BPhen) with an EQE of over 7%. By

examining the steady-state photoluminescence (PL) and electroluminescent (EL) spectra of pure and mixed thin films, it is found that the emission is originated from the exciplex of blend materials. And the transient photoluminescence spectra further proved this point.

2 Experiment

The organic films were deposited by thermal evaporation in a high-vacuum system with a pressure of less than 5×10^{-4} Pa onto quartz plates. Then steady-state PL spectra of the films were monitored by a Perkin Elmer LS 50B luminescence spectrometer. And the PL quantum efficiency was measured by an integrating sphere. The transient PL spectra were detected by Edinburgh FLS920 spectrometer at room temperature. The fabricated devices were grown by thermal evaporation in a high-vacuum system with a pressure of less than 5×10^{-4} Pa without breaking vacuum on glass substrates with 180 nm thickness ITO. The current-voltage-brightness characteristics were measured by using a set of Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. And the EL spectra were measured by a Spectrascan PR650 spectrophotometer.

3 Results and discussion

Figure 1(a) shows the PL spectra of m-MTDATA, BPhen and their mixed films with a molar ratio of 1:1. The

emission peak of the neat films of m-MTDATA and BPhen (chemical structures are seen in Fig. 1(b)) are 432 and 389 nm, respectively, which are obviously blue and violet emissions. When co-depositing the two materials, the PL emission is appeared at 556 nm, which is red-shifted and broaden with respect to the donor and acceptor emission peaks. The origin of the red-shifted and broaden emission should be considered to be the exciplex formed between m-MTDATA and BPhen. From Figs. 1(b) and 1(c), it can be seen that the difference between the highest occupied molecular orbits (HOMO) of m-MTDATA and the lowest unoccupied molecular orbits (LUMO) of BPhen is $5.1 \text{ eV} - 2.8 \text{ eV} = 2.3 \text{ eV}$. Obviously, this value is approximately consistent to the photon energy of the formed exciplex (2.23 eV), indicating that m-MTDATA and BPhen molecules effectively form an exciplex in the excited state. The phosphorescent spectra at 77 K are also shown in Fig. 1(a), where m-MTDATA shows a peak emission at 492 nm and BPhen at 550 nm. Meanwhile, the blend shows the phosphorescent emission centered at 556 nm, which is similar to the its fluorescence spectrum, meaning that it is possible for this blend to present an energy back transfer process from the exciplex triplet state to the exciplex singlet state. The overlaps between the blend and m-MTDATA and BPhen at 77 K are quite large, suggesting there might be energy transfer from the triplet state of m-MTDATA and BPhen to the triplet state of the blend and the back energy transfer from the blend to them are also possible. To distinguish the emission of the exciplex from the emission of m-MTDATA and BPhen, the transient PL spectra were recorded at room temperature for them, as shown in Fig. 2. The transient signals of m-

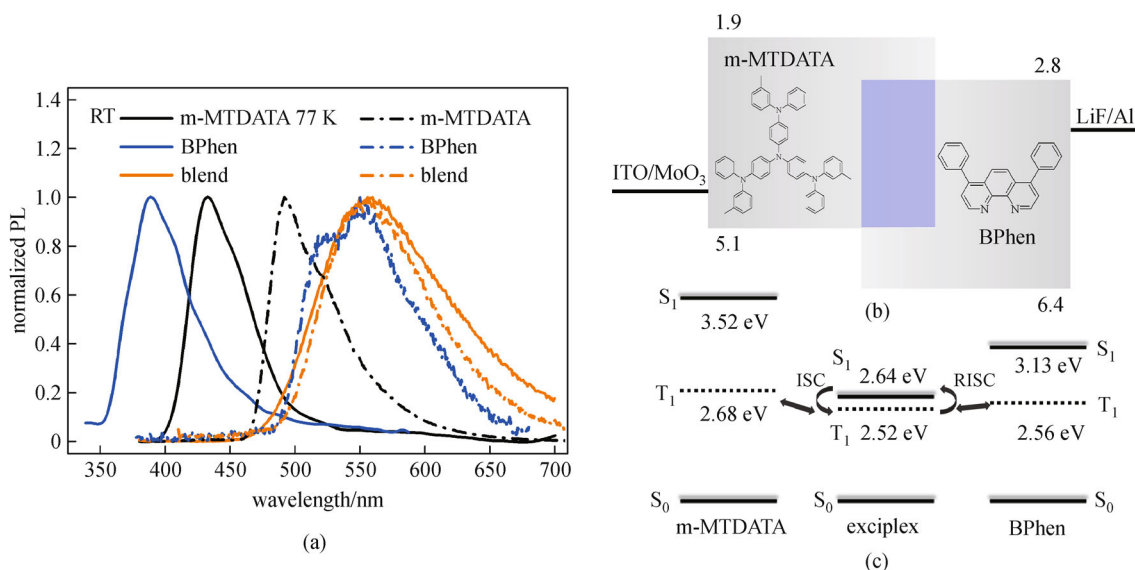


Fig. 1 (a) Normalized PL spectra of m-MTDATA (black line), BPhen (blue line) and m-MTDATA:BPhen (molar ratio of 1:1, orange line) at room temperature (RT) (solid line) and 77 K (dash dot line); (b) schematic diagram of device structure and its energy levels, and the chemical structures of m-MTDATA and BPhen are given in inset; (c) energy levels of m-MTDATA and BPhen, and their exciplex. S₁: singlet; T₁: triplet; S₀: ground state; ISC: intersystem crossing; RISC: reverse intersystem crossing

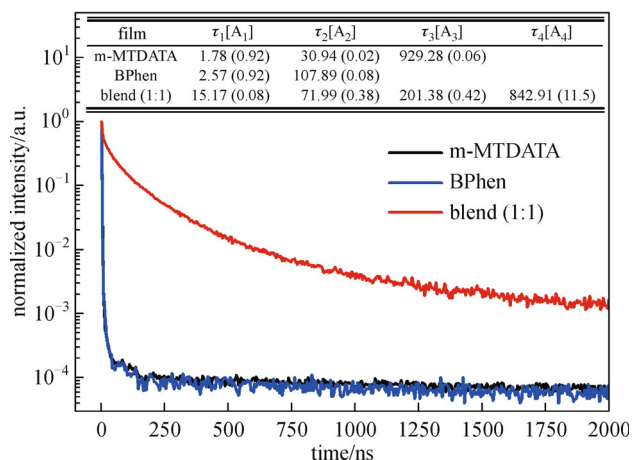


Fig. 2 Transient PL spectra of m-MTDATA (black), BPhen (blue) and m-MTDATA:BPhen (molar ratio of 1:1, red). Inset gives fluorescence decay lifetimes values that are recorded at exciting wavelength of 375 nm (in nanoseconds)

MTDATA and BPhen are similar and show short lifetimes. When they are mixed together, the lifetime is obviously prolonged, which could be ascribed to be the effects of multiple back and forth intersystem crossings between nearly resonant singlet and triplet states. So, the distinction of the exciplex from the pure films in PL transients interprets the different emission mechanisms, and the PL emission of the blend film should come from the exciplex.

To testify the EL properties of the exciplex, we fabricated the simple devices with structure of ITO/MoO₃ (10 nm)/m-MTDATA (65 nm)/m-MTDATA:BPhen (*x*, 40 nm)/BPhen (65 nm)/LiF (1 nm)/Al, where *x* is the molar ratio of m-MTDATA and BPhen, which is 2:1 (device 1), 1:1 (device 2) and 1:2 (device 3). Here we used m-MTDATA as the hole transporting layer and BPhen as the electron transporting layer. The large energy level difference of 1.3 eV between the HOMO levels of m-MTDATA and BPhen, and 0.9 eV between LUMO levels of them makes sure that the injected carriers will be well confined in the emitting layer. Although the PL quantum efficiency of the m-MTDATA:BPhen blend film is only 8.6% at room temperature, which is rather lower than 20% (m-MTDATA:t-Bu-PBD film), 26% (m-MTDATA:3TPYMB film) [9] and 28.5% (m-MTDATA:PPT film) [10], the *EQE* of OLED based on m-MTDATA:BPhen blend is yet over 5%. As shown in Fig. 3(a), the maximum *EQE* of the three devices are 6.5%, 7.0% and 7.3%, all of which exceed the theoretical limit of fluorescent devices. For our fluorescent OLEDs with 8.6% PL efficiency, the maximum *EQE* should be no more than 0.43% (Eq. (1)). Even all the triplets convert to the singlets through TTA, the maximum *EQE* will still be no more than 1.1% (Eq. (2)). So we ascribe the high *EQE* in our devices to the back energy transfer of triplet state to the singlet state of the exciplex, as proven above. Furthermore, we found that the

device 3 shows the highest *EQE*, meaning that the charge carrier balance in emission layer (EML), thus determining the efficiency of exciton recombination and generation, is also very important in the device efficiency. As we know, m-MTDATA shows a hole mobility in the order of 10⁻⁴ cm²/(V·s) [11] and BPhen has an electron mobility of around 10⁻⁴ cm²/(V·s) [12], too, indicating a good charge balance can be achieved in the devices. For the case of device 1 with the molar ratio of 2:1 corresponding a weight ratio of m-MTDATA and BPhen to about 4.8:1, the electrons will be blocked at the interface region between the EML and the electron transporting layer, resulting in narrower recombination region and higher exciton annihilation, thus low efficiency. As the ratio of BPhen in the m-MTDATA:BPhen blend increases, the injected electrons will be transported into the more wide region in EML, thus increasing the recombination width and reducing the exciton annihilation, leading to higher efficiency. The achievement of high efficiency in device 3 can also be further proved by the reduction of efficiency roll-off. The resulted *EQE* of device 2 and 3 can be well fitted by the TTA model [13], as shown in Fig. 3 (solid line). The well fittings indicate that the efficiency roll-off is TTA predominant, which should be originated from the large contribution of the triplet state in the EL emission through a back energy transfer process. The higher critical current density (*J*₀) of 83.3 mA/cm² for device 3 than that of 38.3 mA/cm² for device 2 also indeed means that the TTA in device 3 is greatly improved and the more triplet excitons are used for the emission. As shown in Fig. 3(b), the device 3 also shows higher power efficiency (*PE*), the maximum *PE* reaches 25 lm/W.

Figure 4 shows the EL spectra of the three devices. It is clearly seen that they emit a yellow light at about 560 nm peak wavelength. Obviously, the yellow emission should be from the exciplex emission. The inset of Fig. 4 also gives the EL spectra of device 2 at different voltages, exhibiting good spectrum stability. As seen, the observed EL peaks are slightly red-shifted with respect to the PL spectrum (556 nm). This is because of the enhancement of delayed fluorescence from exciplexes by the electrical excitation, similar to that like in m-MTDATA: t-Bu-PBD and m-MTDATA: 3TPYMB systems [9].

This donor-acceptor system can also be used as the host for phosphor with suitable triplet energy level. Here, Ir (bt)₂(acac) (bis(2-phenylbenzothiazolato-N,C^{2'})iridium (acetylacetonate)) was adopted as yellow phosphor by fabricating the device structure of ITO/MoO₃ (10 nm)/m-MTDATA (65 nm)/m-MTDATA:BPhen: Ir(bt)₂(acac) (8 wt%, 40 nm)/BPhen (65 nm)/LiF (1 nm)/Al, and the molar ratio of m-MTDATA and BPhen blend here is 1:1. Figure 5 (a) shows the current density-voltage-luminance performance, the device exhibits extraordinary low turn-on voltage of 2.1 V, which is lower than the triplet energy of Ir (bt)₂(acac) (2.23 eV) [14] of the device. Such low turn-on voltage should be benefit from the mixed host which

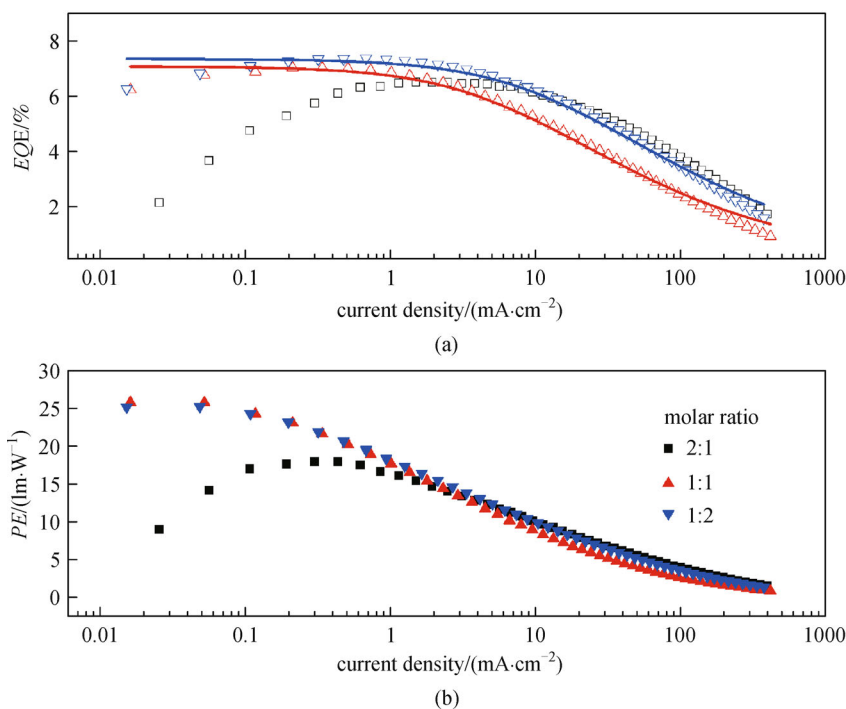


Fig. 3 External quantum efficiencies (*EQEs*) (a) and power efficiencies (*PEs*) and (b) of the device 1 (black square), device 2 (red up triangle) and device 3 (blue down triangle). Solid lines in (a) are the fitting of TTA model

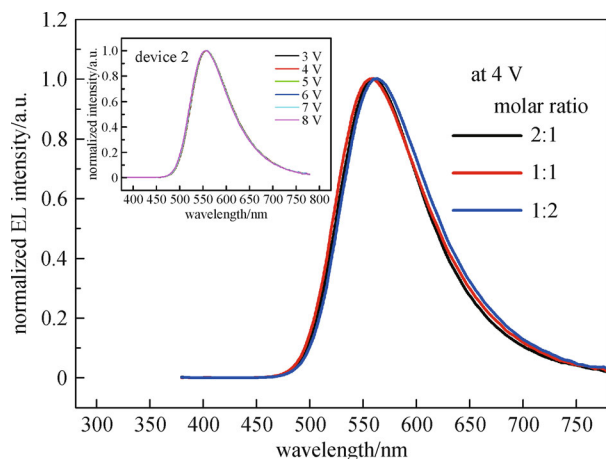


Fig. 4 EL spectra of the three devices at a applied voltage of 4 V. Inset shows the EL spectra of device 2 at applied voltages from 3 to 8 V

provides a zero energy gap from the triplet of host to the dopant, minimizing the energy loss through energy transfer. Since the exciplex host has an equivalent singlet and triplet energy level, the energy loss during inter system crossing should be negligible. The device shows a maximum *PE* and *EQE* of 86.1 lm/W and 20.7%, respectively, which proves the validity of the mixed host. And the EL spectra at Fig. 5(c) depicts a complete Ir (bt)₂(acac) emission at 560 and 600 nm, meaning the thorough energy transfer from host to dopant.

4 Conclusions

In conclusion, we demonstrate high efficiency yellow fluorescent OLEDs based on exciplex emitter. The formation of exciplex results in an effective back energy transfer from exciplex triplet state to its singlet state due to their small energy level difference, which greatly enhances the device efficiency. As a result, the maximum *EQE* is over 7%, and the maximum *PE* reaches 25 lm/W. It is also found that the charge balance in exciplex-based emission layer plays an important role in adjusting the utilization of the formed excitons. Clearly, this emission of exciplex formed by blending or bilayer interface at an electron donor and an electron acceptor has represented a new design to produce high efficiency fluorescence OLEDs [9,10,15,16]. Furthermore, the co-blend systems with exciplex property can also serve as promising materials as a bipolar host for phosphorescence dopant, thus realizing low voltage, high efficiency phosphorescence OLEDs [17–20]. The advantage of exciplex as host for phosphorescence OLEDs is that the exciplex possesses approximately the same triplet level as the singlet one, therefore, both of singlet and triplet energies from the exciplex host can be effectively transferred to the phosphorescence dopant. By simply doping 8 wt% yellow phosphor into the exciplex blend, an extraordinary low turn-on voltage of 2.1 V is achieved, and the maximum *PE* and *EQE* reach 86.1 lm/W and 20.7%, respectively.

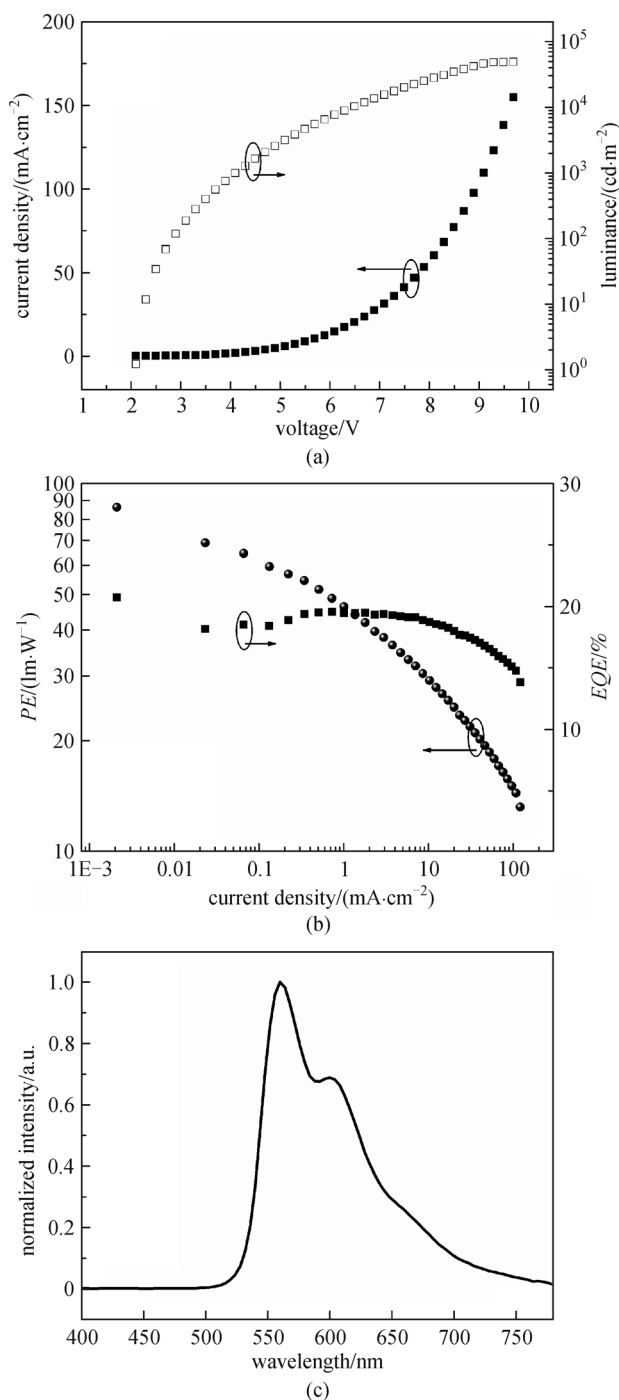


Fig. 5 Performance of Ir(bt)₂(acac) doped device: (a) current density-voltage-luminance properties; (b) power efficiency (*PE*) and external quantum efficiency (*EQE*); (c) EL spectrum at the driving voltage of 5 V

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