

Excimer emission from a novel ethyne-based fluorescent dye in organic light-emitting devices

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Abstract

A novel ethyne-based fluorescent dye, 10-(4-Dimethylamino-phenyl ethynyl)-anthracene-9-carbonitrile (DMAPEAC), emitting orange/red light was employed as the light emission layer in organic light-emitting devices (OLED). The absorption and photoluminescence (PL) peak of DMAPEAC dispersed in methylene chloride were measured to be 480 nm and 600 nm, respectively. On the other hand, DMAPEAC (3 wt.%) dispersed in tris(8-hydroxyquinoline) aluminum (Alq₃) films deposited on fused silica exhibited two PL peaks at 600 nm and 630 nm. The extra PL peak at 630 nm was shown to be due to the excimer formation by absorption measurement. An OLED device with trilayer structure using *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) as the hole transport layer, Alq₃ doped with DMAPEAC as the emission layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as the hole-blocking and electron-injection layer, and lithium fluoride (LiF)/aluminum (Al) as the cathode. A strong exciton energy transfer from Alq₃ to DMAPEAC was observed as revealed by the electroluminescence (EL) and PL spectra. Maximum brightness of 19,400 cd/m² was obtained at 16 V for the device with 1% DMAPEAC in the Alq₃ layer.

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1. Introduction

Since the demonstration of the first heterojunction organic light-emitting devices (OLED) in 1987 by Tang and VanSlyke [1], intense researches have been conducted on the development of OLED due to their potentials in flat-panel displays. The doping of dyes in host materials is often used to modulate the emission wavelength [2–5], enhance the device performance [6,7] and increase the device lifetime [8–10], by energy transfer from host to dye. For full-color applications, it is necessary to develop blue, green and red emitters, with excellent color purity and luminous efficiency. Among them, doping technology is particularly crucial for the red emitter due to the serious concentration

quenching effect in red emission. Therefore, red emitters are rarely deposited as a separate layer. They are more often used as the dopants, and diluted in the host molecules [11]. Tang et al. [2] doped pyran-containing compounds in Alq₃ and successfully tuned the emission peak from green to orange/red (600 nm). They were the first group obtaining red OLED. Pyran-based red OLEDs have since become well known and been extensively studied [4,12,13]. Porphyrin compounds and europium chelate complexes have also attracted intense attention in the last decade [14–17]. The tremendous efforts in modifying the moiety of the above compounds have resulted in the development of new long-wavelength red emitters (>630 nm) with high photoluminescence efficiency and fine color purity. But a new series of compounds with new emission mechanism remains useful for red emission.

In this article, a new ethyne-based luminescent molecule for orange/red emission is demonstrated. Fig. 1 shows the

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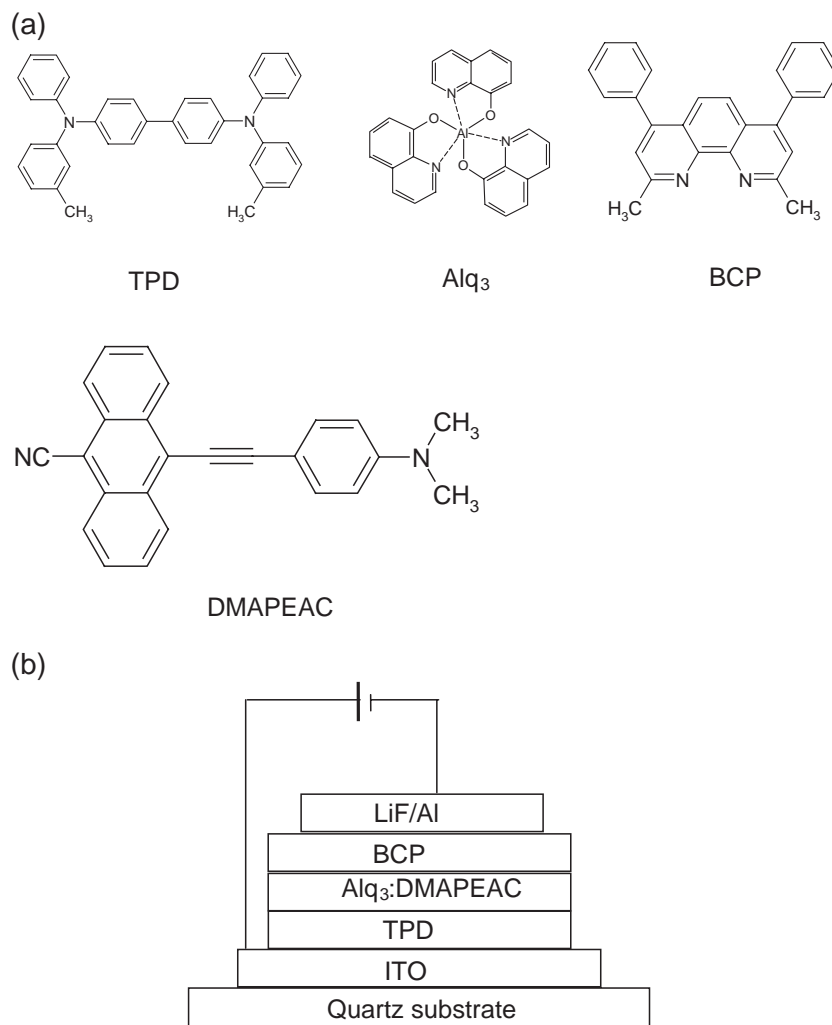


Fig. 1. The structure of OLED device and the species used in this study: TPD, Alq₃, BCP and DMAPEAC.

structure of the novel organic molecule, 10-(4-Dimethylamino-phenyl ethynyl)-anthracene-9-carbonitrile (DMAPEAC), which is different from the three series of compounds mentioned above. DMAPEAC was used as a guest molecule in a host–guest system. Energy transfer and carriers trapping behavior were studied by obtaining the photoluminescence (PL) and absorption spectra of the compound and the electroluminescence (EL) characteristics of the device. Both the emission wavelength and the current–voltage–luminescence (I – V – L) behavior of the device were measured.

2. Experimental details

DMAPEAC was synthesized by coupling the corresponding terminal arylacetylenes with 9-bromo-10-anthronitrile under modified Sonogashira conditions. The synthesis procedures are described in details in reference [18]. The ITO-coated glass substrate (20 Ω/\square , Merck-Taiwan Corp.) was first cleaned by ethanol-impregnated

paper with mechanical rubbing and then cleaned sequentially with de-ionized water, isopropanol, and alcohol. After being loaded into the plasma system with parallel electrodes, the ITO-glass substrate was first treated by oxygen plasma for around 2 min. The substrate was then transferred to a thermal vaporization system with a base pressure of 3×10^{-6} Torr. The *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) (15 nm, Alfa) and tris(8-hydroxyquinoline) aluminum (Alq₃) (50 nm, Alfa) doped with DMAPEAC were then evaporated as the hole transport and the light-emitting layers, respectively. The 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (10 nm, Aldrich) layer was deposited as the hole-blocking and electron-injection layer. The BCP layer was employed to confine excitons, in order to avoid exciton quenching by the cathode. Finally, lithium fluoride (LiF) (1.5 nm) and aluminum (Al) (100 nm) were evaporated as a stable cathode in air. The device structure is shown in Fig. 1. Doping in the host was achieved by co-evaporating both compounds using two independently controlled quartz crystal microbalances. The evaporation rates of the organic

materials, LiF layer, and Al cathode were 0.1–3 Å/s, 0.1 Å/s, and 10 Å/s, respectively. Using a metal mask to define the active area around 5 mm², the I – V – L characteristics of devices were measured by a source meter (Keithley 2400) and a luminance meter (LS-110). Absorption spectra were measured by an ultraviolet–visible spectrometer (Jasco UV-500). Photoluminescence (PL) and electroluminescence (EL) spectra were recorded by a spectrometer equipped with CCD (Jobin-Yvon TRIAX 550). Fused silica substrate was used for PL measurement.

3. Results and discussion

3.1. Optical properties of DMAPEAC

The optical properties of the DMAPEAC in both the liquid solution and the solid films were investigated. Fig. 2 showed the absorption and the PL spectra of DMAPEAC in dilute methylene chloride solution and in thin films (40 nm in thickness) deposited on fused silica. In the methylene chloride solution, DMAPEAC had an absorption maximum at about 480 nm, Fig. 2(a), and a PL peak at around 600 nm, Fig. 2(b). A large Stokes shift (approximately 120 nm) was observed. The large Stokes shift is favorable for preventing the self-absorption of the emitted light in EL devices. However, the PL intensity of pure DMAPEAC film was weak compared with that of DMAPEAC in liquid solution, due to the concentration quenching effect. For a high concentration of light-emitting molecules, the emitted light may be absorbed by neighboring molecules or the excitons are de-excited through energy transfer mechanisms. It is interesting to note that the PL spectra, Fig. 2(c), of the pure DMAPEAC film are different from those, Fig. 2(b), in the dilute solution. An extra peak at 630 nm with high intensity was observed for the pure DMAPEAC film. The peak was attributed to the

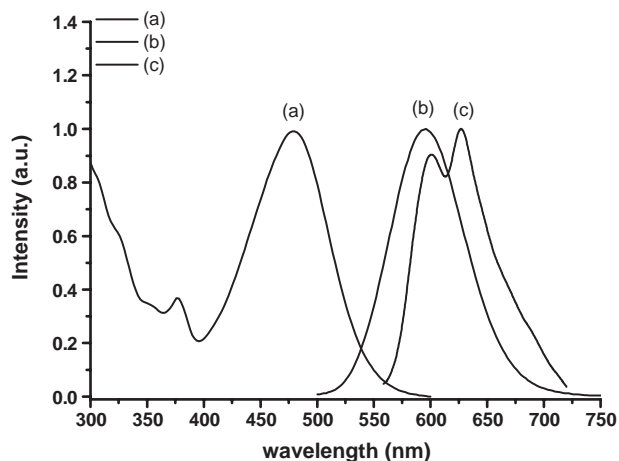


Fig. 2. (a) Absorption and (b) photoluminescence (PL) spectra of the DMAPEAC in dilute methylene chloride solution. (c) PL spectra of the pure DMAPEAC solid film.

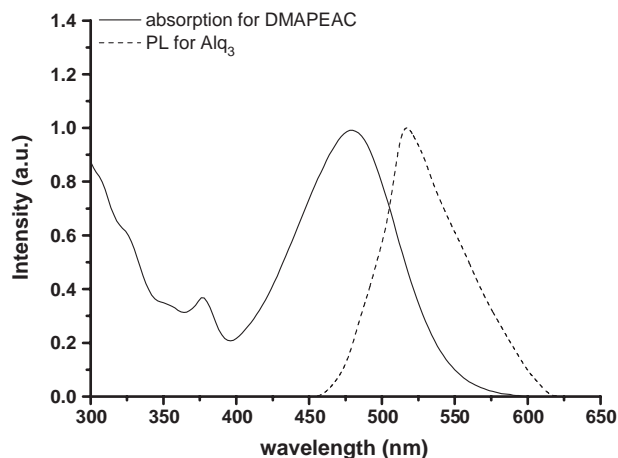


Fig. 3. Absorption spectra of DMAPEAC and PL spectra of Alq₃.

excimer emission [19,20], and will be discussed in the next section.

Due to the serious concentration quenching in film conditions, DMAPEAC had to be diluted in a matrix forming a guest–host system. The exciton energy must be transferred efficiently from the host material to the guest (also called dye or dopant) for light emission to occur. Generally, energy transfer proceeds through Förster and Dexter mechanisms. Förster transfer process involves a long range (40–100 Å) dipole–dipole interaction of donor and acceptor molecules. It is generally observed in a fluorescence doping system. In contrast, Dexter process is a short range interaction by means of charge exchange, and generally observed in a phosphorescence doping system [21]. Förster energy transfer requires the overlap between the emission spectra of a host and the absorption spectra of a guest. Therefore, the choice of proper host material is important for enhancing the device performance. Fig. 3 shows the absorption spectra of DMAPEAC and the photoluminescence spectra of Alq₃. Large overlap between the spectra of Alq₃ and DMAPEAC was observed. Good energy transfer efficiency was expected between the Alq₃ host and the DMAPEAC guest. Therefore, Alq₃ was chosen as the host to study the interaction between Alq₃ and DMAPEAC.

3.2. Photoluminescence of DMAPEAC in Alq₃ film

The PL and absorption spectra of DMAPEAC dispersed in Alq₃ film on the fused silica substrate were measured. PL measurements were performed using an excitation source of 389 nm, corresponding to the maximum absorption of Alq₃ and the minimum absorption of DMAPEAC. PL spectra of the pure Alq₃ and the DMAPEAC-doped Alq₃ films are shown in Fig. 4(a). In the pure Alq₃ films, only one PL peak centered at 520 nm appeared. However, in the doped Alq₃ films, two PL peaks were observed corresponding to 600 nm and 630 nm. The absorption spectra of the pure Alq₃ and the DMAPEAC-doped Alq₃ films are also shown in Fig.

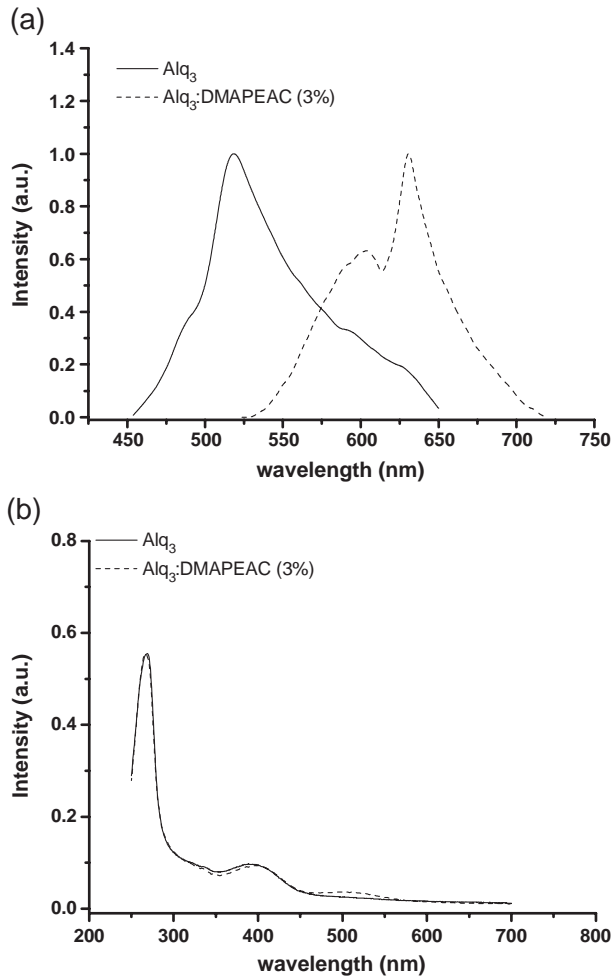


Fig. 4. (a) PL spectra of the Alq₃ film and the DMAPEAC-doped Alq₃ film. (b) Absorption spectra of the Alq₃ film and the DMAPEAC-doped Alq₃ film.

4(b), indicating no difference between both spectra and suggesting that no new compound was formed accounting for the 630 nm PL peak in the doped film. Therefore, the 630 nm peak in PL spectra must be resulted from the formation of charge transfer complexes. Charge transfer complexes, such as exciplexes and excimers, appear only under excitation conditions. Exciplexes are formed by interaction of an excited molecule D*(A*), donor (or acceptor), with its unexcited counterpart A(D), acceptor (or donor). Excimers are formed in the same way as exciplexes, except that the former involves the interaction between the same species (A and A*), and the latter involves interaction between two different species (A* and D, or A and D*). Charge transfer complexes could not be formed in ground state and were unlikely to appear in the absorption spectra, as clearly seen in Fig. 4(b). However, charge transfer complexes may appear in the PL spectra, due to the interaction of the photon-excited molecule with the neighboring ground-state molecule. Therefore, the results in Figs. 2 and 4 suggest that the extra 630 nm PL peak should be due to the formation of excimers. The possibility of

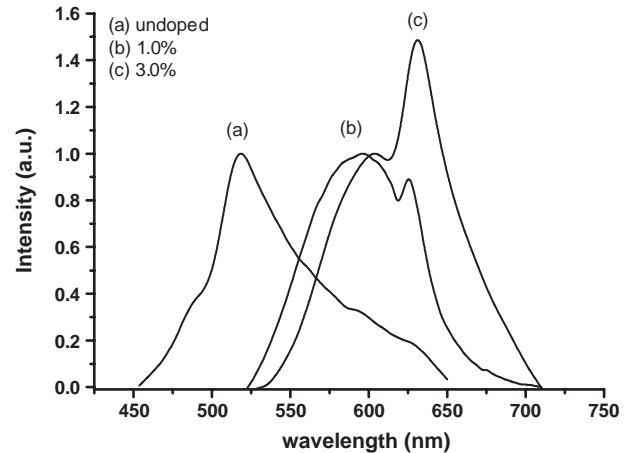


Fig. 5. Electroluminescence spectra of the devices with various concentrations of DMAPEAC in Alq₃.

forming exciplexes between Alq₃ and DMAPEAC is ruled out, since the 630 nm PL peak has been observed in the pure DMAPEAC film.

3.3. Electroluminescence spectra and device characteristics

The devices consisted of ITO/TPD(15 nm)/Alq₃:DMAPEAC (*x*%, 50 nm)/BCP(10 nm)/LiF/Al, where *x* was varied from 0% to 3%. Fig. 5 shows the EL spectra of the devices with various concentrations of DMAPEAC in Alq₃. The undoped device exhibited the green emission of Alq₃ with the peak centered at 520 nm. The device doped with 1% DMAPEAC exhibited a major peak centered at around 600 nm and a very small peak at 630 nm. The EL emission from the host, Alq₃, was completely quenched by DMAPEAC. The full width at half maximum (FWHM) for the EL spectra from the doped device was broader than the undoped device, due to the emission characteristics of DMAPEAC. The EL spectra of the doped device were similar to the PL spectra of DMAPEAC in Alq₃. Hence, high efficiency of Förster energy transfer between Alq₃ and DMAPEAC was observed. By increasing the doping

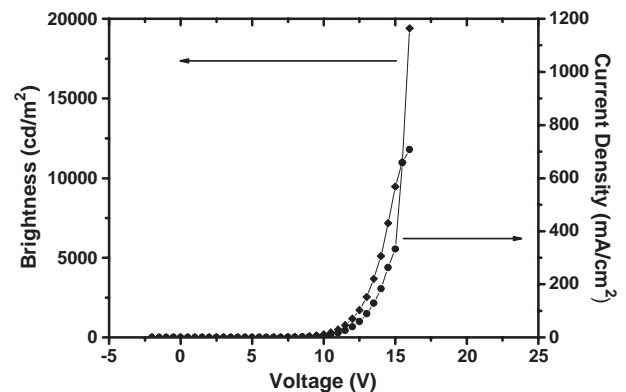


Fig. 6. Current density–Voltage–Luminance (*I–V–L*) curves for the device with the structure of ITO/TPD/Alq₃:DMAPEAC(1%)/BCP/LiF/Al.

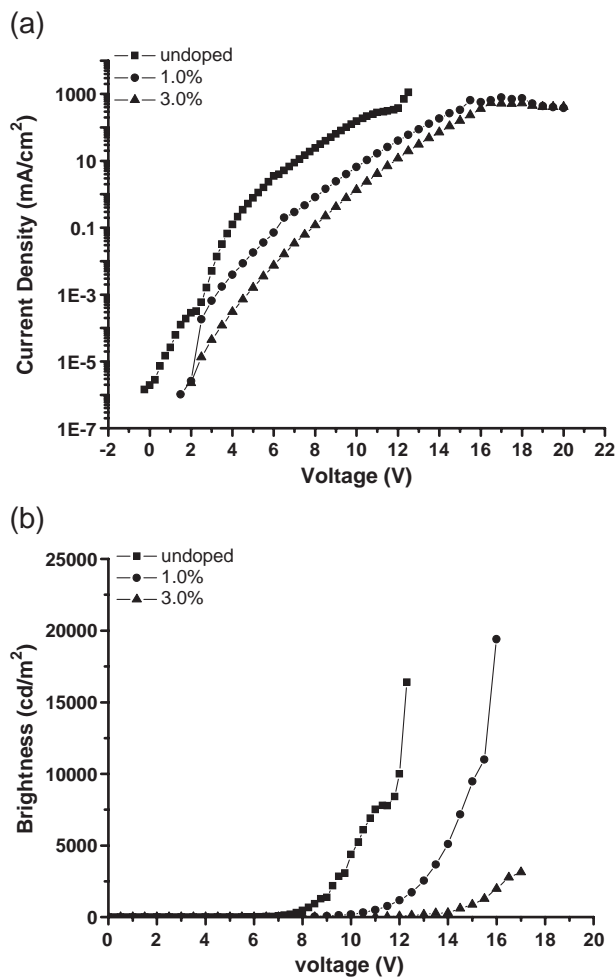


Fig. 7. (a) Current density–Voltage (I – V) and (b) Luminance–Voltage (L – V) curves for the devices with various DMAPEAC concentrations in Alq_3 .

concentration to 3%, the intensity of the excimer emission in EL spectra was increased so greatly that the excimer emission (630 nm) became dominant over the intrinsic emission (600 nm) of DMAPEAC. The dependence of EL spectra on the concentration of dye is typical of excimer emission. The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates of our EL spectra were (0.31, 0.57), (0.54, 0.44) and (0.6, 0.39) for 0%, 1% and 3% doping, respectively. The green emission from Alq_3 was changed to the orange–reddish emission from DMAPEAC. Fig. 6 shows the I – V – L curves of the device with 1% DMAPEAC. The maximum brightness was 19,500 cd/m^2 at a current density of 560 mA/cm^2 and a voltage of 16 V. The device performance was examined by fabricating the devices doped with various concentrations of dye. Fig. 7 shows the I – V – L curves for devices with various dye concentrations. The device performance degraded with increasing the dye concentration. The poor performance at a high concentration of dye should be due to the effects of concentration quenching and high concentrations of excimers formed. By increasing the doping concentration, the current density

across the device was decreased, likely due to the effect of carrier trapping. Further investigation was in progress by fabricating the hole-only and electron-only devices to determine whether the hole trapping or electron trapping mechanism is the dominant one.

4. Conclusions

High efficiency excimer emission was observed from a novel ethyne-based fluorescent dye, 10-(4-Dimethylamino-phenylethynyl)-anthracene-9-carbonitrile (DMAPEAC). High energy transfer efficiency between Alq_3 and DMAPEAC was observed for the device exhibiting high EL efficiency. EL emissions from Alq_3 were completely quenched by doping 1% DMAPEAC in Alq_3 . An extra peak at 630 nm, besides the intrinsic peak of DMAPEAC at 600 nm, was observed due to the excimer emission in both the PL and EL spectra. The maximum EL luminance of the device with DMAPEAC-doped Alq_3 could reach almost 20,000 cd/m^2 at 16 V and 560 mA/cm^2 . The Commission Internationale de l'Éclairage (CIE) chromaticity coordinate was (0.54, 0.44) for 1% DMAPEAC in Alq_3 . Both the concentration quench and the excimer formation were observed at low doping levels (1%).

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