White organic light-emitting diodes based on a combined electromer and monomer emission in doubly-doped polymers*

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We report on white organic light-emitting diodes (WOLEDs) based on polyvinylcarbazole (PVK) doped with 1,1-bis((di-4-tolylamino)phenyl)cyclohexane (TAPC) and perylene, and investigate the luminescence mechanism of the devices. The chromaticity of light emission can be tuned by adjusting the concentration of the dopants. White light with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.33, 0.34) is achieved by mixing the yellow electromer emission of TAPC and the blue monomer emission of perylene from the device ITO/PVK: TAPC: perylene (100:9:1 in wt.) (100 nm)/tris-(8-hydroxyquinoline aluminum (Alq_3) (10 nm)/Al. The device exhibits a maximal luminance of 3727 cd/m^2 and a current efficiency of 2 cd/A.

Keywords: white organic light-emitting diodes, electromer emission, monomer emission, Commission Internationale de L'Eclairage (CIE)

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention because they are very promising for use in large-area flat panel displays, and the flexibility of the organic materials makes it possible to potentially use them for flexible displays.[1−4] Polymers and small molecules have been utilized in OLEDs and various colours throughout the visible spectrum have been achieved. White emission is important because of its potential application in full colour displays, backlights, and lighting sources. The most common approaches to generating white light in white OLEDs (WOLEDs)[5−7] are to use multilayer structures and multiply-doped structures. The EL spectra of multilayer devices depend on both the thickness of each organic layer and the applied voltage. In multiply-doped WOLED, white light is generated by doping a primary or complementary colour emitting dyes in a polymer or molecule layer. However, incomplete energy transfer from a higher energy host or dopant to a lower energy dopant often leads to undesired energy transfer, which leads to the change in the spectral characteristic of the device.

On the other hand, of particular interest are OLEDs based on bimolecular excited species including excimer, exciplex, electromer, and electroplex because a red-shifted, broad band EL from these species has been observed.[8,9] Excimer, exciplex, electromer, and electroplex have been used to reduce the number of emissive dopants and achieve a balanced white light.[10−12] This approach prevents the cascade of energy from a host or a higher energy dopant to a lower-energy dopant, avoiding the colour balancing problem caused by intermolecular interactions in multiply-doped WOLEDs.[6,13] Electromer emission is attributed to spatially cross recombination of nearest-neighbour electron–hole pairs of chemically identical molecules charged by electrons and holes. A strong electromer emission band at 580 nm was found in films of 1,1-bis((di-4-tolylamino)phenyl) cyclohexane

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(TAPC),[14] which might be used to produce white light in OLEDs.

In the present paper, we report on the fabrication of WOLED based on doubly-doped polyvinylcarbazole (PVK), in which the yellow emission comes from an electromer of TAPC and the blue emission originates from a monomer of perylene,[15] and investigate the EL mechanism of the devices.

2. Experiment

We fabricated the devices with an indium–tin–oxide structure (ITO)/PVK: TAPC: Perylene/tris-(8-hydroxyquinoline aluminum (Alq_3)/Al. The PVK was doped with perylene, the TAPC acted as the emissive layer, and Alq_3 acted as an electron transfer layer (ETL). The doubly-doped PVK was first spin-coated on ITO with a sheet resistance of 20 Ω/square which had been pre-cleaned by successive ultrasonic solvents of ethanol, acetone, and deionized water. Then, the ETL was deposited by thermal evaporation at a vacuum of 10^{-6} Pa. Finally an aluminum layer was evaporated as a cathode to complete the device. The active area of the device was 7 mm^2. The absorption spectra were collected with Shimadzu 3101PC UV-Vis-NR absorption spectrometer. The EL and PL spectra were recorded by a Spex Fluorolog-3 spectrometer. The current–voltage–luminance (I–V–L) characteristics were measured by a PR650 spectrophotometer (Photo Research) and a Keithley 2410 source-meter.

3. Results and discussion

Figure 1 shows the normalized EL spectrum of the PVK film and the absorption spectra of the perylene and TAPC films. PVK exhibits an EL band centred at 420 nm. There is a large overlap between the EL spectrum of PVK and the absorption spectrum of perylene, implying that a strong Förster energy transfer[15,16] can occur from PVK to perylene. However, an energy transfer from PVK to TAPC can hardly occur because there is little overlap between the absorption spectrum of TAPC and the EL spectrum of PVK. The EL spectrum of perylene in PVK is also shown in Fig. 1. No emission from PVK is observed because of the complete energy transfer from PVK to perylene while perylene exhibits an EL band with two peaks at 455 nm and 480 nm, and a shoulder at 520 nm due to its monomer emission.[15] It can be seen that there exists no energy transfer between perylene and TAPC because there is no overlap between the EL spectrum of perylene and the absorption spectrum of TAPC. The energy level diagram in the inset of Fig. 1 also indicates the excitation energy of PVK can be efficiently transferred to perylene since the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of perylene[15] are located inside the energy band gap of PVK, while the energy transfer from perylene to TAPC is impossible because the energy band gap of perylene is smaller than that of TAPC[17], and an energy transfer from PVK to TAPC hardly happens because they have very close energy band gaps.

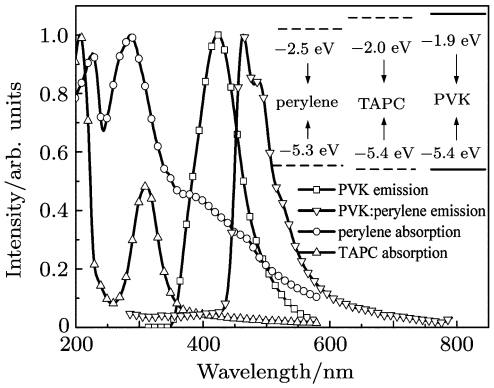


Fig. 1. Normalized EL spectra of the films of PVK and PVK: perylene (100:1 in wt.) and the absorption spectra of the perylene and TAPC films. The inset shows the energy level diagrams of PVK, perylene, and TAPC.

We obtain white light by combining the blue emission of PVK with the yellow emission of TAPC. Firstly, the ITO/PVK: TAPC (100:x in weight (wt))/Al (x = 2, 3, 4) devices are fabricated and their normalized EL spectra are shown in Fig. 2. There are two broad emission bands: one at 420 nm and the other at 580 nm. The former is from PVK and the latter is ascribed to electromer emission, resulting from the direct cross recombination transition between electrons and holes trapped on tritolylamine (TTA) subunits of different TAPC molecules.[14] Figure 2 also shows that the intensity of the blue emission is much higher than that of the yellow emission even if the concentration ratio of TAPC increases, indicating that white emission cannot be achieved in the TAPC-doped PVK system.

Therefore, an appropriate blue-emitting dopant is needed to achieve white light in the devices based on TAPC-doped PVK. Perylene[15] is commonly used as a blue fluorescent dopant. The efficient energy

transfer from PVK to perylene combined with no energy transfer between perylene and TAPC will avoid pronounced variation in colour with applied voltage. White emission is expected from the combined electormer emission of TAPC and the monomer emission of perylene.

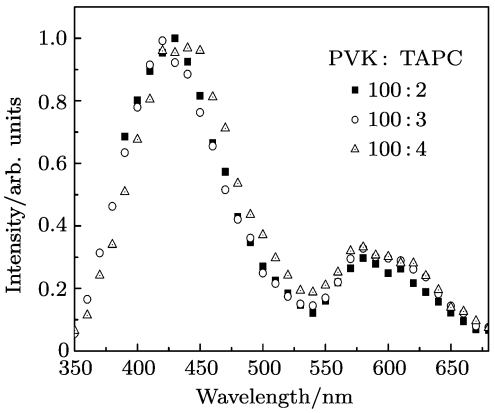


Fig. 2. Normalized EL spectra of the devices ITO/PVK: TAPC (100:x in weight.) (100 nm)/Al (x = 2, 3, 4) at 20 V.

In order to know the emission properties and the proper concentration of perylene in PVK, the devices ITO/PVK: perylene (100:x in wt.)/Al (x = 1, 2, 3, 4, 5, 10) are investigated. The EL spectra of the devices are similar to the PL spectra of the corresponding PVK: perylene thin films, as displayed in Fig. 3 show emission peaks at 455, 480, and 520 nm. No emission band at 420 nm is observed, indicating that complete energy transfer occurred from PVK to perylene. The identical peak positions for the EL and the PL indicate that the three emission peaks all originate from the characteristics of perylene monomer emission and no exciplexes form between PVK and perylene. The intensity of the 525-nm peak increases while those of the two bands before 500 nm decline as the concentration of perylene increases and the position of the peak shifts toward longer wavelengths. This bathochromic shift is caused by the solid state solvent effect.[18] Consequently, we choose 100:1 as the weight ratio of PVK: perylene to avoid the bathochromic shift and obtain the blue emission from perylene.

Finally we doubly dope PVK with perylene and TAPC to obtain white light. A series of devices ITO/PVK: TAPC: perylene (100:x:1) (100 nm)/Alq_3(10 nm)/Al (x = 1, 5, 6, 7, 8, 9, 10, 20, 30) was studied in order to carefully adjust the concentration of TAPC. Here Alq_3 plays two important roles: one is to transport electrons,[15,19,20] since it has high electron mobility[21] and its LUMO energy level lies between the LUMO energy level of PVK and the work

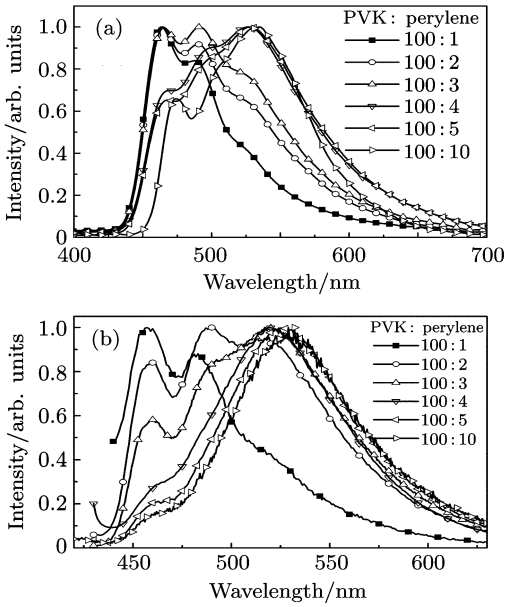


Fig. 3. (a) Normalized EL spectra of the devices ITO/PVK: perylene (100:x in wt.) (100 nm)/Al (x = 1, 2, 3, 4, 5, 10) at 26 V. (b) Normalized PL spectra of the corresponding PVK: perylene thin films excited at 355 nm.

function of aluminum; the other is to prevent cathode-induced luminescence quenching.[22] It is found that the possible concentration ratios of TAPC for realizing a white emission range from 100:5:1 to 100:10:1. Figure 4(a) displays the normalized EL spectra of the devices with the concentration ratios of TAPC in a range from 6 to 9 (the others are not shown here) and their corresponding Commission Internationale de L'Eclairage (CIE) coordinates. No obvious emission from Alq_3 is observed. The emission peaks at 455 nm and 480 nm, and the shoulder at 520 nm originating from the monomer of perylene which is exited by energy transfer from PVK, and the broad emission band at 580 nm comes from the electromer of TAPC which is excited by direct carrier trapping. The device in which the weight ratio of PVK: TAPC: perylene is 100:9:1 emits a balanced white light and its CIE coordinates of (0.33, 0.34) at 24 V are very close to the white light equal energy point. The I–V–L characteristics of the device are shown in Fig. 4(b). The luminance reaches 3727 cd/m^2 at 30 V and the current efficiency is 2 cd/A. The inset of Fig. 4(b) shows the dependence of the EL spectrum on applied voltage implying that the spectral characteristic changes with the increase of the voltage. This can be explained by different luminescence mechanisms of perylene and TAPC in PVK and different dependences

of their quantum efficiencies on applied voltage.[14,15] The CIE coordinates change within a range between (0.27, 0.32) and (0.39, 0.36) as the voltage increases from 18 V to 32 V, which are in the white light area of the CIE chromaticity diagram.

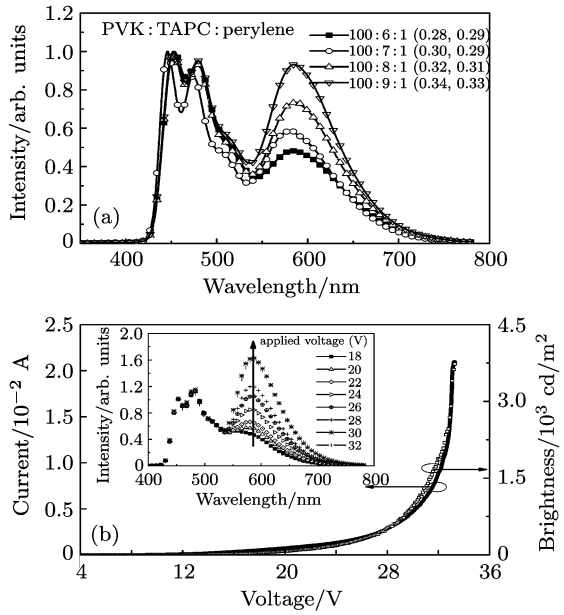


Fig. 4. (a) Normalized EL spectra of the devices ITO/PVK: TAPC: perylene (100:x:1 in wt.) (100 nm)/Alq3 (10 nm)/Al (x = 6, 7, 8, and 9) at 24 V and the corresponding CIE coordinates. (b) I–V–L characteristics of the device ITO/PVK: TAPC: perylene (100:9:1 in wt.) (100 nm)/Alq3 (10 nm)/Al. The inset shows the dependence of the EL spectrum of the device on applied voltages.

4. Conclusions

We demonstrate WOLEDs based on electromer emission of TAPC and monomer emission of perylene in PVK. TAPC excited by direct carrier trapping emits an electromer emission band at 580 nm, and perylene exited by energy transferred from PVK emits two monomer emission peaks at 455 nm and 480 nm, and a shoulder at 520 nm. The concentration ratio of the dopants must be carefully balanced in order to obtain a white emission. White light with CIE coordinates of (0.33, 0.34) is obtained in the device ITO/PVK: TAPC: perylene (100:9:1 in wt) (100 nm)/Alq_3 (10 nm)/Al. The device has a maximal luminance of 3727 cd/m^2, and the current efficiency is 2 cd/A.

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