White organic light-emitting diodes based on electroplex from polyvinyl carbazole and carbazole oligomers blends*

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(Received 17 May 2009; revised manuscript received 22 September 2009)

White organic light-emitting diodes with a blue emitting material fluorene-centred ethylene-liked carbazole oligomer (Cz6F) doped into polyvinyl carbazole (PVK) as the single light-emitting layer are reported. The optical properties of Cz6F, PVK, and PVK:Cz6F blends are studied. Single and double layer devices are fabricated by using PVK: Cz6F blends, and the device with the configuration of indium tin oxide (ITO)/PVK:Cz6F/ tris(8-hydroxyquinolinate)aluminium (Alq_3)/LiF/Al exhibits white light emission with Commission Internationale de l'Éclairage chromaticity coordinates of (0.30, 0.33) and a brightness of 402 cd/m^2. The investigation reveals that the white light is composed of a blue–green emission originating from the excimer of Cz6F molecules and a red emission from an electroplex from the PVK:Cz6F blend films.

Keywords: white organic light-emitting diodes, electroluminescence, electroplex

PACC: 7800, 7860F, 7280L

1. Introduction

Organic materials have been widely used in electroluminescent (EL)[1] and photovoltaic cells[2] in the last two decades. Especially, white organic light-emitting diodes (WOLEDs) have attracted much attention due to their potential applications, such as full colour display through colour filters, backlights for liquid crystal displays, and solid lighting sources.[3−5] Many techniques have been developed to obtain white light emission from small-molecule and polymer based light-emitting diodes. For the devices based on small molecules, the most general approach is to fabricate multi-layer devices by sequentially evaporating multiple emissive layers under high vacuum, where each layer emits a primary colour.[4−7] But this approach is somewhat complicated in the device fabrication and it is also difficult to control the balance of the recombination of holes and electrons in each layer to achieve white light emission. Compared with multi-layer WOLEDs, single-layer polymer based devices can be fabricated facilely by wet processes, including spin-casting, screen printing, and ink-jet printing techniques. However, quite a limited number of materials that emit white light as a single polymer have been developed.[8−10] Recently, long-wavelength emissions of some materials have been observed in their electroluminescence spectra but not in their photoluminescence (PL) spectra, which have mostly been assigned to emissions from a so-called electromer or electroplex and discussed in terms of phosphorescence or direct radiative recombination of holes and electrons residing at two neighbouring molecules.[11−14] Li *et al.*[15] reported on a single-emitting-component WOLED fabricated from 1,3,5-tris(2-(9- ethylcarbazyl-3)ethylene)benzene (TECEB) molecule. The EL emission of the molecule is white, which differs significantly from the PL emission. The EL emission in the blue region originates from the singlet excited state of the individual molecule, and that in the green and red region produced only by electric excitation arises from the electromer. Chen *et al.*[16] found a long-wavelength EL emission, which was absent in the PL spectra, from polyfluorenes grafted with cyclometalated iridium complexes and charge transport moieties. This additional long-wavelength emission should be contributed from a possible cross re-

*Project supported by the National Basic Research Program of China (Grant No. 2009CB623605), the National Natural Science Foundation of China (Grant No. 50673035), Program for New Century Excellent Talents in Universities of Ministry of Education, the 111 Project (Grant No. B06009).

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combination between the main-chain fluorene units and the side-chain carbazole units, i.e. an electroplex. These studies indicated that it was a simple and efficient way to use the long-wavelength emission of the electromer or electroplex to achieve white light.

Our previous studies showed that carbazole oligomers with certain modifications can emit long-wavelength emission under electric excitation.[17] In the present paper, we continue to investigate these materials and fabricate a WOLED, by using a novel blue light-emitting fluorene-centred ethylene-linked carbazole oligomer (Cz6F) (see Fig. 1) doped with PVK as a light-emitting layer and tris(8-hydroxyquinolinate)aluminium (Alq_3) as an electron transport layer. The light from the diode is pure white with Commission Internationale de l'Éclairage (CIE) coordinates of (0.30, 0.33). The investigated PL and EL properties of Cz6F and PVK:Cz6F blend system show that the white light emission is composed of blue–green emission from the Cz6F excimer and long-wavelength emission from the electroplex between PVK and Cz6F under electric field.

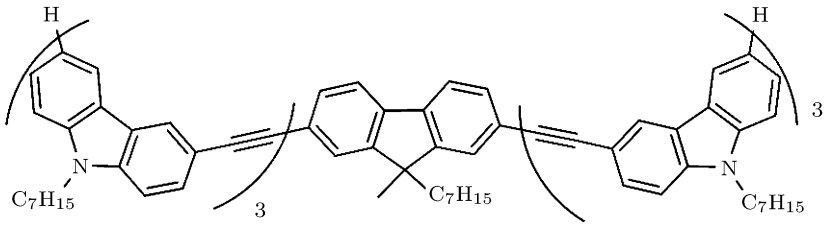


Fig. 1. Scheme of the molecular structure of Cz6F.

2. Experiment

The synthesis and the characterization of fluorene-centred ethylene-linked carbazole oligomers (Cz6F) have been described in our previous work.[17] Poly-(3,4-ethylenedioxythiophene):poly-(styrenesuphonic acid) (PEDOT:PSS) was purchased from Bayer AG, PVK and Alq_3 were purchased from ACROS and used without further purification. UV–vis absorption spectra were recorded by a UV-3100 spectrophotometer. Fluorescence measurements were carried out by RF-5301PC. The film for PL experiments was prepared on pre-cleaned quartz plates in air atmosphere.

Indium-tin-oxide (ITO)-coated glass with a sheet resistance of 20 $\Omega\cdot cm^{-2}$ was used as substrate. The ITO glass was routinely cleaned in an ultrasonic cleaning bath with detergent solutions, rinsed with acetone, boiled in isopropyl alcohol, rinsed with methanol, and then with de-ionized water in sequence. The PEDOT:PSS was spin-coated on the pre-cleaned ITO glass substrates and then the PEDOT:PSS layer was dried in a vacuum oven at 80 °C for 20 min. The active layers were spin-coated at a speed of 1500 r/min on the top of the PEDOT:PSS layer from a 5 mg/mL chloroform solution of PVK:Cz6F mixtures. The electron-transporting layer Alq_3 was deposited by thermo-evaporation. The OLEDs were completed by vapour depositing Al as the cathode through a mask. The EL spectra, luminance CIE coordinates and the current–voltage–luminance characteristics of the devices were measured with a rapid scan system by using a Photo Research PR650 spectrophotometer and a computer-controlled, programmable, direct-current (DC) source. All measurements were carried out at room temperature under ambient atmosphere.

3. Results and discussion

3.1. Optical properties

The PL emission spectra of Cz6F in chloroform solutions with different concentrations and in film are shown in Fig. 2. The PL emission peaks of Cz6F in dilute solution are located at 407 nm and 430 nm, corresponding to the emissions of an individual Cz6F molecule. When the concentration of the solution is increased, both peaks become weaker, and a new emission peak appearing at 470 nm becomes stronger and red-shifted, indicating aggregation of the molecules. Also, the PL spectrum of Cz6F in highly concentrated solution shows only one broad peak, which is quite similar to the peak emitted by Cz6F in film. This is because the distance between the planar Cz6F

molecules decreases with the gradual increase of solution concentration, resulting in the enhancement of the $\pi - \pi$ interaction between molecules and the formation of an excimer. Therefore, when the concentration is increased, the emission from single molecules decreases and the new emission peak at 470 nm from the excimer becomes dominant. Hence, the emission peak of the film of Cz6F originates from the emission of excimer states.

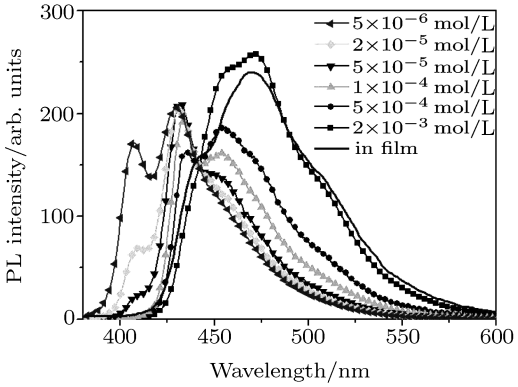


Fig. 2. PL spectra of Cz6F in $CHCl_3$ solutions with different concentrations and in film.

Figure 3 shows the absorption and PL spectra of the films of pure Cz6F, PVK, and PVK:Cz6F with a dopant concentration of 50%. The absorption spectrum of PVK:Cz6F blend film is a simple superposition of the absorption spectra of PVK and Cz6F monomer which indicates that there is no interaction between PVK and Cz6F molecules in their ground states. The emission of the PVK:Cz6F blend film is very similar to that of Cz6F film, which comes

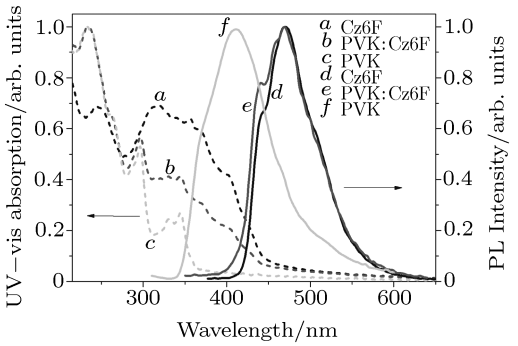


Fig. 3. UV–vis absorption and PL spectra of the films of Cz6F, PVK and Cz6F doped PVK with a concentration of 50%.

from the Cz6F excimer. Because the PL spectrum of PVK overlaps with the absorption spectrum of Cz6F from 340 nm to 450 nm, it is expected that efficient energy transfer from PVK to Cz6F could happen.[18]

3.2. Electroluminance properties

In order to study the EL properties of PVK:Cz6F blend film, a double-layer EL device A was fabricated with a structure of ITO/PEDOT:PSS/PVK:Cz6F/Alq_3/Al, where PVK:Cz6F blend film with a dopant concentration of 50% was used as a hole-transporting and emitting layer, while Alq_3 was used as an electron-transporting layer. The EL spectra of device A driven by different voltages, shown in Fig. 4, differs significantly from the PL spectrum of PVK:Cz6F blend film. When the applied voltage increases, the device exhibits a white EL spectrum with the long-wavelength emissions around 600 nm being much stronger and the spectrum covering the whole visible range. The emission in the blue region which resembles the PL spectrum of Cz6F film evidently originates from the excimer of Cz6F, which is formed via hole-electron recombination in the PVK:Cz6F blend film.[12,18] The emission in the long-wavelength region around 600 nm does not appear in the PL spectra of PVK:Cz6F blend film or pure Cz6F film, indicating that the long-wavelength emission is a peculiar characteristic of EL of the blend film. The EL emission is an almost pure white emission with Commission Internationale de l'Éclairage (CIE) coordinates of (0.30, 0.33) under a driving voltage of 19 V.

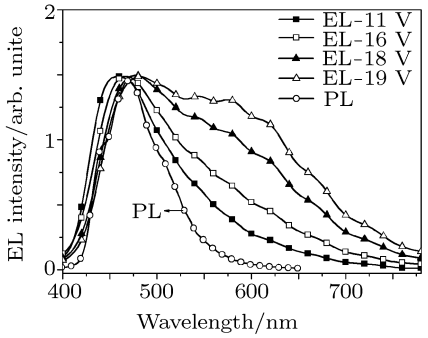


Fig. 4. EL spectra of ITO/PEDOT:PSS/PVK:Cz6F/Alq_3/Al device under various voltages.

The current density–voltage–brightness characteristics of the double-layer device are shown in Fig. 5, which illustrates a turn-on voltage of 6 V (with a brightness of 1 $cd \cdot m^{-2}$) and a maximum brightness of 402 $cd \cdot m^{-2}$ at 16 V. Furthermore, the double-layer device shows a maximum current efficiency of 0.1 $cd \cdot A^{-1}$.

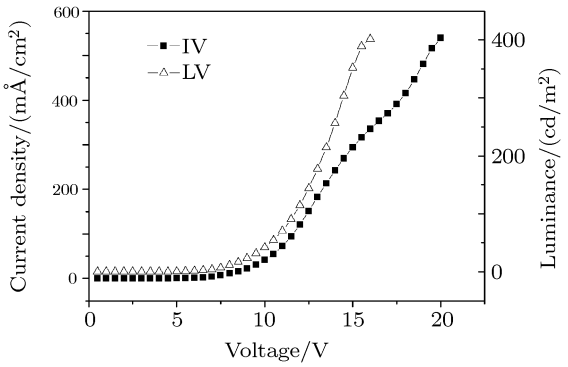


Fig. 5. Current density–voltage–brightness characteristics of ITO/PEDOT:PSS/PVK:Cz6F/Alq_3/Al device.

Obviously, the long-wavelength emission around 600 nm of the above double-layer device is produced only by electric excitation. To explain the origin of the long-wavelength emission in the double-layer device, two single-layer devices, whose structures were ITO/PEDOT:PSS/PVK:Cz6F/Al with a dopant concentration of 50% /0.2% were fabricated and served as devices B and C, respectively. Figure 6 shows the EL spectra of the two single-layer devices under different voltages. The EL spectrum of device A operated at 19 V is also included in Fig. 6 for comparison. The features of the EL spectra of devices A and B are similar to and also significantly different from the PL spectra of the blend film. It rules out the possibility that the long-wavelength EL emission from PVK:Cz6F blend film originates from the species at the interface such as an exciplex at the PVK:Cz6F/Alq_3 interface. Additionally, the EL spectra of device C with 0.2% dopant concentration show quite different EL spectra compared with those of devices A and B. There are two independent peaks: one locates at 430 nm in the blue region, and the other appears at 600 nm in the long-wavelength region. On the other hand, the PL spectrum of PVK:Cz6F blend film with 0.2% dopant concentration shows a peak at 430 nm which is very similar to the PL spectrum of Cz6F dilute solution. It demonstrates that 0.2% dopant concentration is too low for Cz6F molecules to interact with each other and thus the PL emission of the blend film originates from the single Cz6F molecule. Accordingly, the EL spectrum with emission at 430 nm of device C resembles the PL spectrum of the Cz6F single molecule, which originates from the excited state of the Cz6F single molecule. The emission in the long-wavelength region at a high applied voltage should result from the interaction between Cz6F and PVK molecules.[12,19,20] A single-layer device with pure Cz6F film as an emitting layer was also fabricated, but it had only an emission peak around 470 nm and no emission in the long-wavelength region of EL spectrum under a low electric field. The EL spectra of pure Cz6F film were not achieved under a higher electric field, because of the bad quality of Cz6F spin-coating film and the unbalanced charge transport inside the device. The identical white light emissions in both the single-layer and the double-layer devices imply that the emission originates from the PVK:Cz6F blend film, while the Alq_3 serves only as an electron transport layer. Accordingly, we infer that the emissions in the long-wavelength regions around 600 nm in devices A and B with high dopant concentrations may arise from the electroplex.[16,22−24]

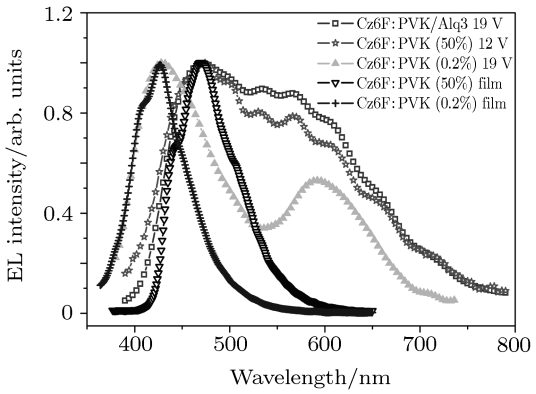


Fig. 6. EL spectra of three devices at various voltages.

To better understand the origin of the emission in the long-wavelength regions, the energy level of Cz6F was calculated from an oxidation-reduction potential which was measured by the cyclic voltammetric method at room temperature.[1)] Figure 7 shows the energy levels of PVK and Cz6F in the device. The highest occupied molecular orbital (HOMO) energy levels of PVK and Cz6F are estimated to be −5.8 eV and −6.1 eV, respectively. The lowest unoccupied molecular orbital (LUMO) of PVK and Cz6F are estimated to be −2.2 eV and −3.3 eV, respectively.[25] According to Refs. [22]–[24], the long-wavelength emission was assigned to the electric-field-induced complex, the electroplex. In the cases of PVK and Cz6F, the electroplex can be regarded as a pair of independent Cz6F and PVK molecules, which is in an excited state formed between complementary molecules carrying a charge (an excess hole, another electron) under electric excitation. The energy of such a hole–electron

[1)] The electrochemical behaviours of Cz6F were examined by cyclic voltammetry in 0.1 mol/dm^3 TBAP/CH_2Cl_2 solution at a scan rate of 100 mV·s^{-1}. On the basis of the roughly evaluated onset oxidation potentials (E^{ox}_{onset}), the HOMO energy level of Cz6F is estimated as −6.10 eV (HOMO = (E^{ox}_{onset}+4.7) eV). The LUMO energy level of Cz6F is −3.30 eV.

pair trapped by two neighbouring molecules should be lower than that of the singlet excited state of a single molecule. As a result, direct cross recombination of the hole located at PVK and the electron at Cz6F under electric field would lead to a new emission at long wavelength compared with the emission of the PL of PVK:Cz6F blend film. It is interesting to note that the white light emission of PVK:Cz6F blend film in our experiments was detected only at a high dopant concentration under electric excitation.

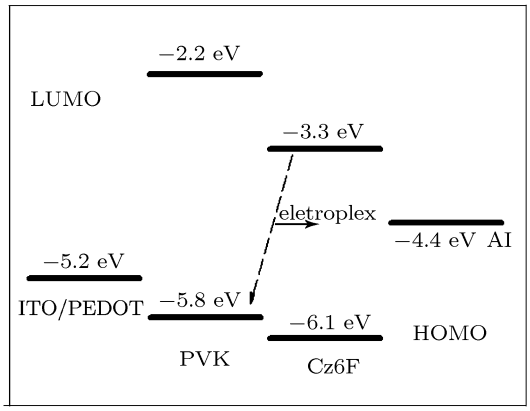


Fig. 7. Energy levels of Cz6F and PVK in the device.

4. Conclusion

PVK:Cz6F blend film is capable of emitting white light in a single emitting layer EL device. The white light emission consists of the blue–green emission from Cz6F excimer and the long-wavelength emission from the electroplex between PVK and Cz6F under electric field. The double-layer EL device fabricated from the PVK:Cz6F blend film with 50% dopant concentration exhibits a pure white light with CIE coordinates of (0.30, 0.33), a maximum brightness of 402 cd· m^{-2}, and a maximum current efficiency of 0.1 cd·A^{-1}, respectively.

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