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The effect of DCJTB concentration on the photoluminescent and electroluminescent properties of PVK–PBD–perylene–DCJTB thin films

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The paper reports a study of photoluminescent (PL) and electroluminescent (EL) properties of PVK–PBD–perylene–DCJTB thin film with variation of DCJTB doping concentrations. Poly(9-vinylcarbazole) (PVK) functioned as polymeric hole-transporting host, 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD) as electron-transporting molecule, perylene as blue dopant, and 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) as a red dopant. The relative intensity of the blue emission from perylene decreased and that of the red emission from DCJTB increased with the increase of DCJTB concentration in both PL and EL spectra. However, the EL spectrum showed stronger DCJTB emission compared to the PL spectrum at the same DCJTB doping concentration, due to the carrier trapping effect. Interestingly, white light emission with C.I.E. coordinates of (0.31, 0.36) was observed in the EL spectrum when 0.05 wt. % of DCJTB was doped into PVK–PBD–perylene blend film. As a result, PVK–PBD–perylene–DCJTB thin film has potential application in white organic light emitting diodes.

Key words: *photoluminescence; electroluminescence; perylene; DCJTB; OLED*

1. Introduction

An organic light emitting diode (OLED) is a thin film device in which the emitting organic material is sandwiched between two electrodes. It emits light when a current is passed through it. OLEDs, using either small molecules or polymers, have attracted considerable interest due to their easy processability, flexibility, low cost, low operating voltages, wide viewing angles, tunability of the colour emission, fast response time, and ease of forming large areas [1, 2].

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Recently, white OLEDs have attracted intense interest due to their potential applications in full colour displays combined with a colour filter, in backlights for liquid crystal displays as well as general illumination purposes. White emission from an OLED can be obtained by mixing two complementary colours (e.g., blue and orange) or three primary colours (red, green, and blue) where different emitting components are stacked in a multilayer structure [3, 4] or mixed within a single layer by doping or blending [5–7]. The latter approach is preferred because of its relatively simple fabrication and relatively stable colour coordinates with respect to the bias voltage.

Although much research has addressed the fabrication of white OLEDs utilizing blue polymer host doped with an orange-red dopant, few studies on dual fluorescent dyes white OLEDs have been reported [5, 6]. Park et al. reported OLEDs fabricated by co-doping perylene and 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl -9-enyl)-4H-pyran (DCJTB) into poly(methylphenylsilane) (PMPS) [8]. However, no white light emission was observed from their devices. In this paper, poly(9-vinylcarbazole) (PVK), one of the most frequently used polymeric hosts due to its excellent film-forming and hole-transporting properties, was used as a host for perylene and DCJTB. Since PVK is mainly hole-transport material, possessing very limited electron-transport capabilities, it is expected that in a single-layer structure, due to the highly unbalanced transport properties of holes and electrons, the recombination of carriers will be inefficient and the carrier recombination zone will also be closer to the cathode where the luminescence quenching occurs [9]. Therefore, an electron-transporting agent, 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD) was blended with PVK to improve the charge balance in the emitting layer [10].

The paper reports a study of photoluminescent (PL) and electroluminescent (EL) properties of PVK–PBD–perylene–DCJTB thin film with various DCJTB doping concentrations.

2. Experimental

The host polymer PVK, having a high weight-average molecular weight of 1 100 000 g/mol, electron-transporting molecule, PBD, blue dopant, perylene and the hole buffer material, PANI-EB were purchased from the Aldrich Chemical Company. The red dopant, DCJTB was purchased from the E-light Corporation. All materials were used as received without further purification. Molecular structures of the materials used in this study are shown in Fig. 1.

In order to study the EL property of PVK–PBD–perylene–DCJTB thin films, typical OLEDs with ITO/PANI-EB/PVK–PBD–perylene–DCJTB/Al structure were fabricated as shown in Fig. 2. The ITO-coated glass substrates were etched and patterned to serve as an anode. The substrates were each cleaned with 2-propanol and acetone in an ultrasonic bath for 15 min. It has been reported that the use of non-doped polyaniline (emeraldine base), PANI-EB as the insulating layer between ITO and the emitting layer resulted in significant reduction of the operating voltage [11].

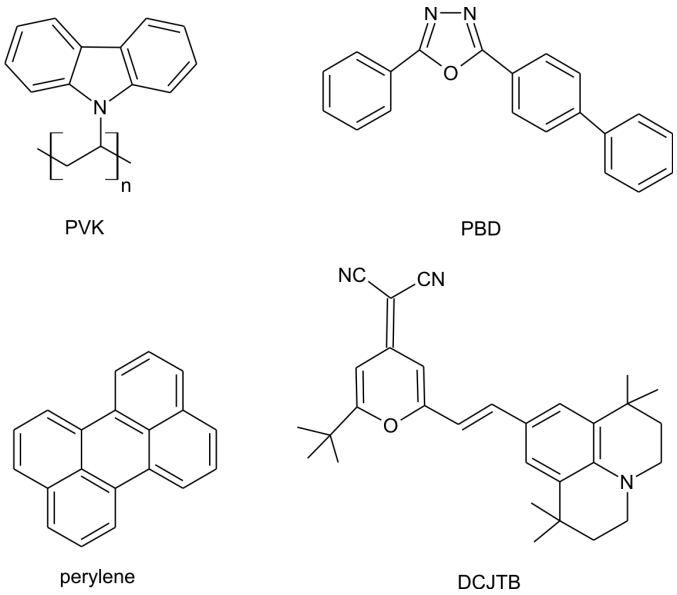

Fig. 1. Chemical structures of the organic materials used

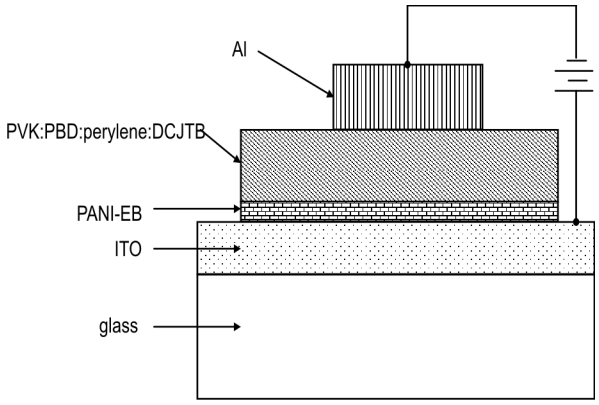

Fig. 2. The OLED with ITO/PANI-EB/PVK–PBD–perylene–DCJTB/Al structure

PANI-EB dissolved in dimethyl sulfoxide (DMSO) was spin-coated onto the ITO-coated glass substrates with a typical spinning speed and time of 2000 rpm for 40 s. After having been spun onto the substrates, the resulting PANI-EB films were dried in a vacuum oven at 80 °C for 30 min to remove excess solvent. 1,2-dichloroethane solutions each containing 8 mg/mL of PVK and PBD were prepared. For a precise doping of the host (PVK–PBD) with a very small amount of the dopants (3 wt. % of perylene and 0.025-0.25 wt. % of DCJTB), the dopants were first dissolved homogeneously in 1,2-dichloroethane. After that, the precalculated portions of the solutions were mixed with the host. The weight percentage of perylene and DCJTB (wt. %) was determined as the ratio of perylene and DCJTB to PVK. The solutions were then spin-coated onto

PANI-EB with a typical spinning speed and time at 2000 rpm for 40 s. The polymer film thickness was about 100 nm as determined by using a scanning electron microscope. Lastly, 150 nm aluminium was deposited as a cathode by using the electron gun evaporation technique.

The absorption and photoluminescence (PL) properties were investigated by depositing the corresponding thin films on pre-cleaned quartz substrates with a Perkin Elmer LAMBDA 900 UV-VIS spectrophotometer and a Perkin Elmer LS55 luminescence spectrometer, respectively. In addition, a Keithley 238 source measurement unit was used to measure the electrical characteristics of the devices, while the EL spectra were obtained with an Ocean Optic HR2000 spectrometer. All organic thin film preparation and measurements were carried out at ambient atmosphere.

3. Results and discussion

Figure 3 shows the absorption spectra of PVK–PBD host, perylene (1 wt. % in PMMA) and DCJTB (1 wt. % in PMMA) thin films. The maximum absorption wavelength for PVK–PBD, perylene and DCJTB was 298 nm, 439 nm and 505 nm, respectively. On the other hand, Figure 4 shows the PL spectra of the organic materials used. The emission of PVK–PBD, perylene and DCJTB peaked at 429 nm, 457 nm and 606 nm, respectively.

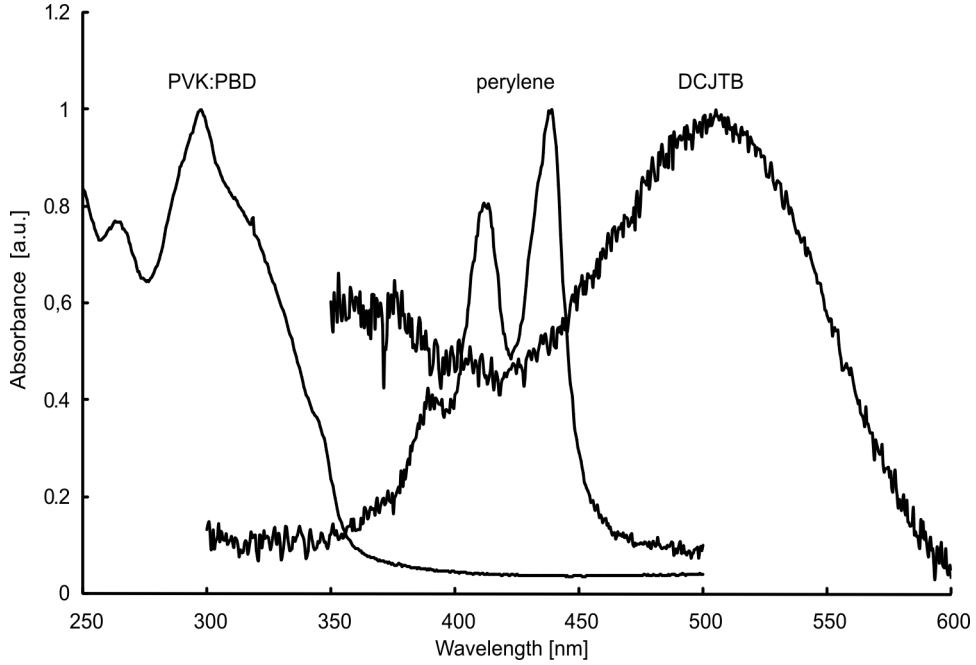

Fig. 3. UV-Vis absorption spectra of the PVK–PBD film, PMMA–1 wt. % perylene film, and PMMA–1 wt. % DCJTB film

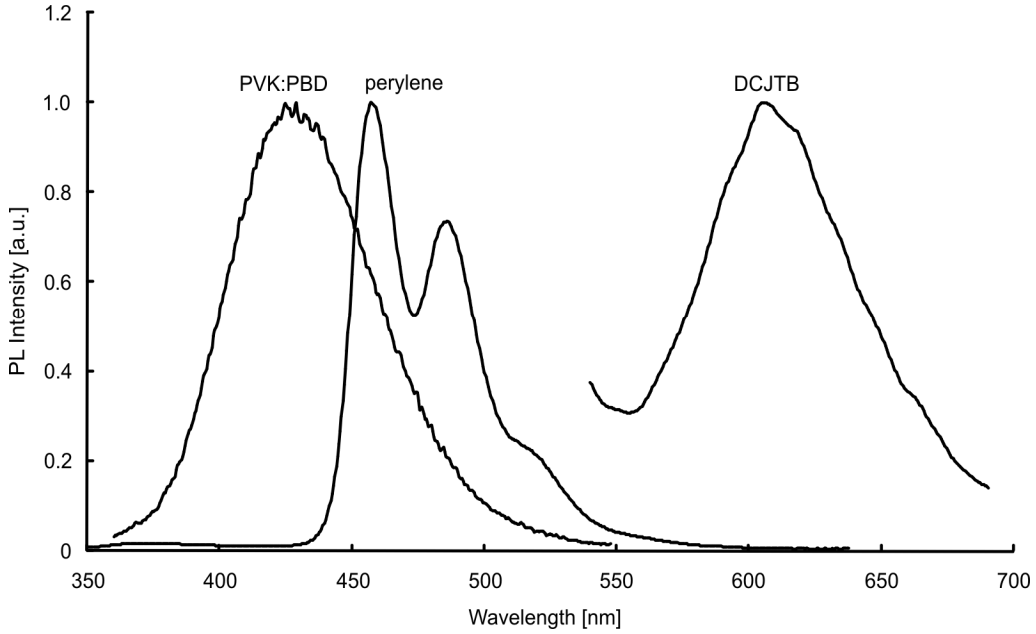

Fig. 4. Photoluminescence (PL) spectra of the PVK–PBD film, PMMA–1 wt. % perylene film, and PMMA–1 wt. % DCJTB film

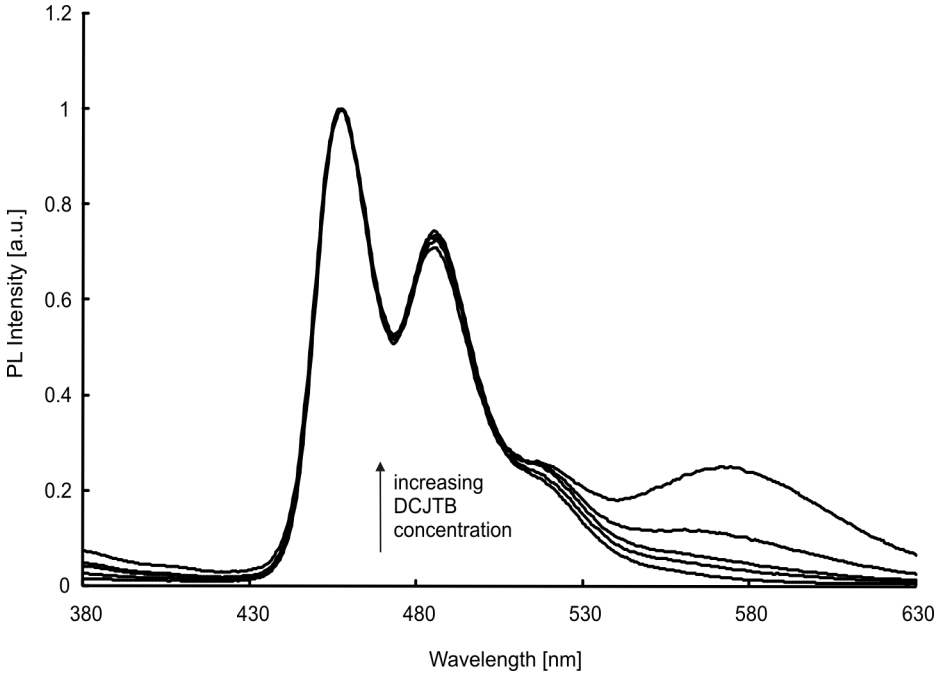

Fig. 5. PL spectra of PVK–PBD–3 wt. % perylene–DCJTB films with various DCJTB doping concentrations

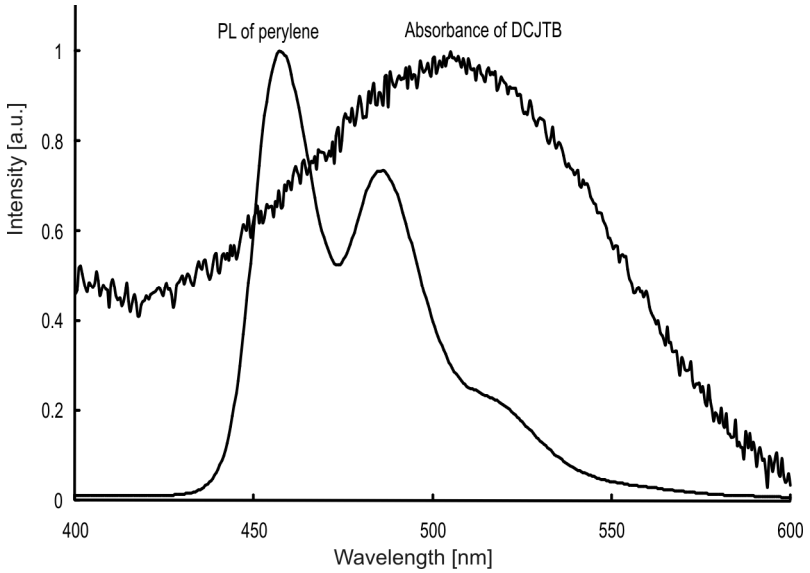

Fig. 6. Spectral overlapping between absorption of PMMA–1 wt. % perylene film and PL of PMMA–1 wt. % DCJTB film

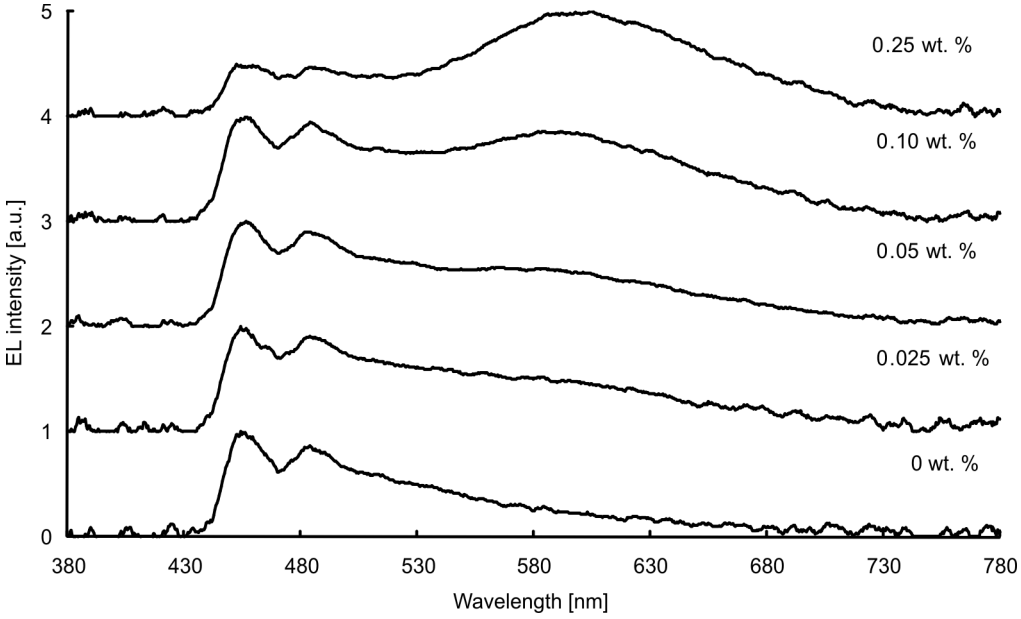

Fig. 7. EL spectra of devices with various DCJTB doping concentrations at 24 V

The PL spectra of PVK–PBD–3 wt. % perylene–DCJTB films with various DCJTB doping concentrations are shown in Fig. 5. The excitation wavelength of the spectra was 330 nm, which lies above the absorption onset of PVK–PBD and only

little absorption by perylene and DCJTB will take place at the point as is shown in Fig. 3. For a device without DCJTB, almost all emission was from perylene even though almost all excited energy was absorbed by PVK–PBD. This indicates that the energy transfer from the host to perylene was nearly complete. Exciton formation under photoexcitation in a guest emitter could result from radiative energy transfer or non-radiative energy transfer from the host. Radiative energy transfer normally can be neglected in emitter-doped OLED systems because it is a relatively slow and inefficient process [12]. Besides, Dexter energy transfer is a dominant mechanism in triplet–triplet energy transfer which can be observed in phosphorescent-based OLED [13, 14]. As a result, the most likely energy transfer mechanism between different molecular species in this study was Forster-type energy transfer [12, 15, 16]. In the case of DCJTB-doped devices, there are two emission bands in the spectra: a blue band from perylene and a red band from DCJTB. The absorption spectrum of DCJTB partially overlaps with the PL spectrum of perylene (Fig. 6), which implies a possibility of the Forster-type energy transfer from perylene to DCJTB [8]. The red band increased with the increase of DCJTB concentration from 0.025 to 0.25 wt. %. The probability for excitation transfer from perylene to DCJTB not only depends on the energy overlapping between them, but also on their spatial distance [17]. As the concentration of DCJTB was reduced (molecules of DCJTB decreased as well), the spatial distance between perylene and DCJTB became larger. As a result, less energy from perylene could be transferred to DCJTB.

Figure 7 shows the EL spectra of the devices with various doping concentrations of DCJTB at an applied voltage of 24 V. With increasing DCJTB concentration, the relative intensity of the blue emission decreased and that of the red emission increased, which indicates more energy from perylene transferred to DCJTB. The trend was similar to that observed in the PL spectra. The incomplete energy transfer from perylene to DCJTB at lower concentration of DCJTB enables the production of white light emission through control of the blend ratio. Figure 8 gives the C.I.E. coordinates of (0.24, 0.33), (0.30, 0.36), (0.31, 0.36), (0.36, 0.38) and (0.44, 0.40) for 0, 0.025, 0.05, 0.10, and 0.25 wt % DCJTB-doped devices, respectively. Among all the EL devices tested in this experiment, the device using the 0.05 wt. % DCJTB exhibited the C.I.E. coordinates (0.31, 0.36) closest to the standard CIE coordinates for white light emission (0.33, 0.33). Obviously, this is a fairly white emission. Importantly, the emission spectrum remained in the white emission region for DCJTB doping concentration from 0.025 wt. % to 0.10 wt. %.

It was also found that the shapes of EL spectrum are different from those of PL spectrum at the same DCJTB doping concentration. For example, at 0.25 wt. % DCJTB loading level, PL from DCJTB was quite low, but for EL the emission from DCJTB was very strong. This phenomenon is common in the doped systems. The main reason for the observation of this phenomenon lies in the different excitation mechanisms of PL and EL. The PL spectra are excited by photons. There is no carrier injected in this process, the emission spectra of a doped system are only determined by

the energy transfer. However, in EL spectra, besides energy transfer, carrier trapping also plays an important role [18–20]. This also can be deduced from the energy level scheme, as shown in Fig. 9 [7, 21, 22]. Since the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy levels of DCJTB are located inside the energy gap of other materials, some of the electrons and holes will be trapped or even directly injected and recombine directly in DCJTB molecules when an electric field is applied.

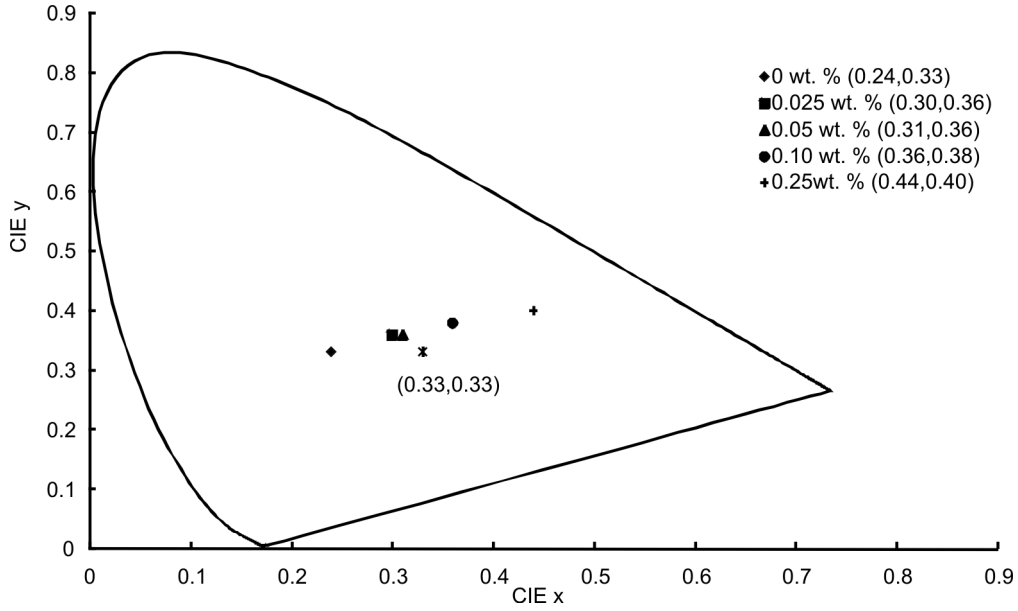

Fig. 8. CIE coordinates of devices with various DCJTB doping concentrations at 24 V

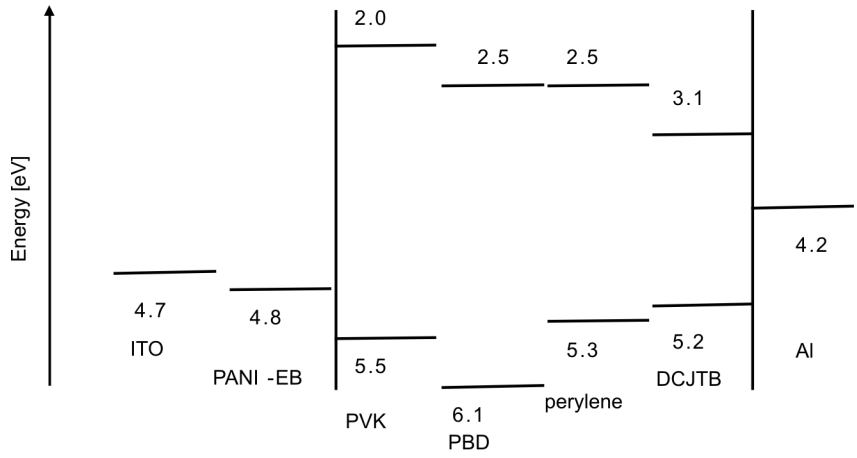

Fig. 9. Energy level diagram of ITO/PANI-EB/PVK–PBD–perylene–DCJTB/Al device

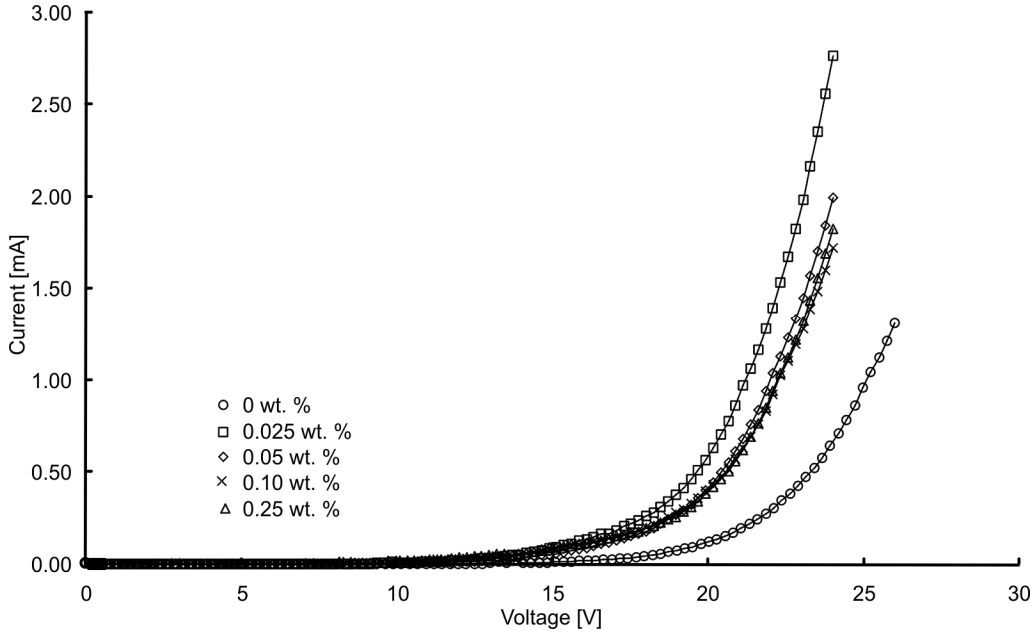

Fig. 10. Current–voltage characteristics of devices at various DCJTB doping concentrations

Figure 10 shows the current-voltage characteristics of the white light emitting devices at room temperature. The forward current was found to increase with increasing forward bias voltage, and the curve has the same characteristics as those of a typical diode. In general, current turn-on voltages for DCJTB-doped devices are lower than those for devices without DCJTB. The current turn-on voltage for DCJTB-doped devices was around 15 V. DCJTB can facilitate both electron and hole injection into the blend layer in the OLEDs due to their lower LUMO and higher HOMO relative to the work function of the Al and ITO, respectively, as shown in Fig. 6. Besides high current turn-on voltage, the luminance of the devices was also very low (< 1 cd/m^2) due to a high energy barrier for electron injection at the cathode-emitting layer interface (1.7 eV). After optimizing the structure of the devices such as adjusting the thickness of emitting layers and the blend ratio of PVK and PBD, using a low work function metal cathode, such as Ca, and introducing electron injection layers etc., further reduction in turn-on voltage and increase in luminance are expected [22–24].

4. Conclusion

The relative intensity of the blue emission from perylene decreased and that of the red emission from DCJTB increased with the increasing of DCJTB concentration in both PL and EL spectra. However, stronger DCJTB emission was observed in the EL spectrum compared to the PL spectrum at the same DCJTB doping concentration due

to carrier trapping effect. Interestingly, white light EL emission with C.I.E. coordinates of (0.31, 0.36) was achieved when 0.05 wt. % of DCJTB was doped into PVK–PBD–perylene blend film. Clearly, PVK–PBD–perylene–DCJTB thin film is suitable to be used as emitting layer in white OLEDs.

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