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# Effects of Doping in Organic Electroluminescent Devices Doped with a Fluorescent Dye

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## Abstract

The effect of doping on the energy transfer and charge carrier trapping processes has been studied in organic light-emitting diodes (OLEDs) doped with a fluorescent laser dye. The devices consisted of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine (TPD) as a hole transporting layer, tris(8-hydroxyquinoline) aluminum ($Alq_3$) as the host, and a fluorescent dye, 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-8-yl)vinyl]-4H-pyran) (DCM2) as the dopant. Temperature dependence of the current-voltage-luminescence (I-V-L) characteristics, the electroluminescence (EL) and photoluminescence (PL) spectra are studied in the temperature ranging between 15 K and 300 K. The emission from DCM2 was seen to be much stronger compared with the emission from $Alq_3$, indicative of efficient energy transfer from $Alq_3$ to DCM2. In addition, the EL emission from DCM2 increasd with increasing temperature while the emission from the host $Alq_3$ decreased. The result indicates that direct charge carrier trapping becomes efficient with increasing temperature. The EL emission from DCM2 shows a slightly sublinear dependence on the current density, implying the enhanced quenching of excitons at high current densities due to the exciton - exciton annihilation.


**Keywords** : organic light-emitting diodes, electroluminescence, energy transfer

## 1. Introduction

Efficient organic electroluminescent devices (OELDs) have attracted a great deal of interest due to their potential application to full-color, flat-panel displays [1,2]. Doping of highly luminescent fluorescent or phosphorescent dyes into the active luminescent layer has been shown to be very effective in improving the luminescence efficiency of OLEDs [3-5]. C. W. Tang et al. have studied in detail the electroluminescence (EL) properties of OLEDs consisting of aluminum (III) tris(8-hydroxyquinoline) ($Alq_3$) as the host and fluorescent dyes [3]. The concentration of the dopant strongly influences the EL spectrum and the efficiency of the doped devices. The EL efficiency decreases due to the concentration quenching at high dopant concentrations where aggregate formation provides nonradiative recombination sites [6,7]. Therefore, the device efficiency device is optimised at a dopant concentration of about 1~2 % for fluorescent dyes [3]. An exciton formed in a host material can transfer its energy to a guest dye molecule through Förster or Dexter energy transfer processes [6]. In addition, an electron or a hole injected from cathode and anode, respectively, can be trapped in the guest molecule, leading to a direct exciton formation on the guest molecule. Since the energy transfer and carrier trapping processes strongly influence the EL efficiency, it is very important to understand these processes in order to improve the performance of the doped OLEDs.

In this work, we have studied the effect of doping on the energy transfer and charge carrier trapping in the multilayer OLEDs consisting of N,N′-diphenyl-N,N′-

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bis(3-methylphenyl)-1,1-biphenyl-4,4′-diamine (TPD) as a hole transporting layer, tris(8-hydroxyquinoline) aluminum ($Alq_3$) as the host, and a fluorescent dye, 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-benzo[i,j]quinolizin-8-yl)vinyl]-4H-pyran) (DCM2) as the dopant. Fig. 1 shows the schematic device structure and the molecular structures of organic materials. The current-voltage-luminescence (I-V-L) characteristics, the electroluminescence (EL) and photoluminescence (PL) spectra were studied in the temperature ranging between 15 K and 300 K. The doped devices showed a bright red emission (peak at ~ 620 nm) with high luminous efficiency. We found that the emission from DCM2 was much stronger compared with the emission from $Alq_3$, indicating of efficient energy transfer from $Alq_3$ to DCM2. In addition, the EL emission from DCM2 increased with increasing temperature while the emission from the host $Alq_3$ decreased, indicating that direct charge carrier trapping becomes efficient with increasing temperature.

## 2. Experiments

The devices were fabricated by using successive vacuum-depositions of TPD (600 Å), $Alq_3$ doped with DCM2 (2 weight %, 300 Å), $Alq_3$ (300 Å) and the Al cathodes on indium tin oxide (ITO) substrates. The evaporation system used a specially designed sample holder with a shutter that allows us to change masks without breaking vacuum. Thus, we could simultaneously fabricate two independent devices, for example, the doped and undoped devices while keeping all other parameters the same. This helps us to avoid the uncertainties arising from different evaporation processes for different devices. The TPD, $Alq_3$ and DCM2 were purchased from H. W. Sands, Aldrich, and SynTec, respectively, and used as received. The evaporation rates for TPD, $Alq_3$ and Al were about 1 Å/s, measured by a quartz crystal oscillator, under a base pressure of about $4x10^{-6}$ Torr. The nominal value of DCM2 doping concentration in $Alq_3$ was controlled by monitoring the evaporation rate of each material with the other material masked by a shutter. The ITO substrates with a sheet resistance of about 10 Ω/□ were supplied by Samsung Corning Inc. The overlap area of the Al and ITO electrodes was about 4 $mm^2$.

The devices were mounted on to a cold finger of cryostat under vacuum. The I-V-L characteristics and the EL spectra were measured in the temperature ranging between 15 K and 300 K with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a calibrated Si photodiode or an ARC P2 PMT through an ARC 275 monochromator. The PL was measured after photoexcitation with a pulse from a dye/$N_2$ laser at wavelength of 400 nm. The PL transient signal, detected by a fast photomultiplier tube, was digitized with a 500 MHz digital storage oscilloscope (Tektronix TDS 644B).

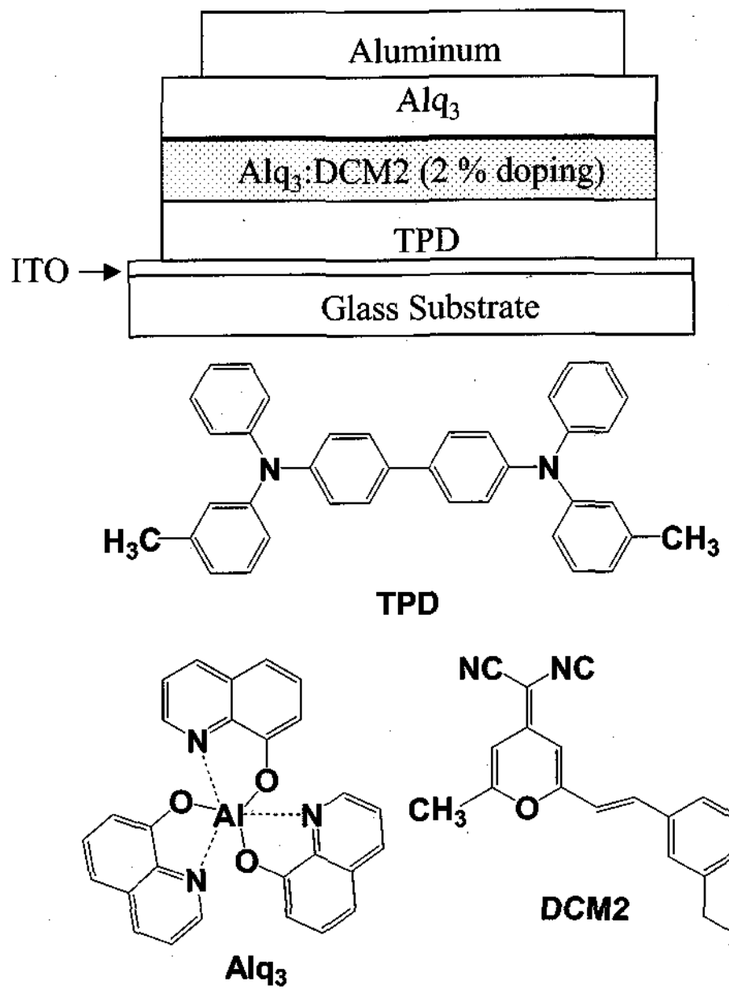


**Fig. 1.** The schematic device structure and the molecular structures of organic materials.

## 3. Results and Discussion

Fig. 2 shows the I-V-L characteristics of ITO/TPD (600 Å)/ $Alq_3$:DCM2 (2 %, 300 Å)/$Alq_3$ (300 Å)/Al and ITO/TPD (600 Å)/$Alq_3$ (600 Å)/Al devices. The EL emission onsets at lower bias voltage, about 3 V for the doped device compared with about 5 V for the undoped device. The inset compares the luminance-current (L-I) dependence of the two devices. By comparing the slope of the L-I curve, which is proportional to the EL quantum efficiency of the devices, we know that the EL quantum efficiency of the doped device is about 3.5

times higher than the undoped device. The I-V-L characteristics showed a power-law dependence on the voltage, as expected from the trap-limited current [8,9]. It was observed that the I-V characteristics were unaffected by the doping of DCM2 with a small quantity although the EL quantum efficiency increased for the doped devices.

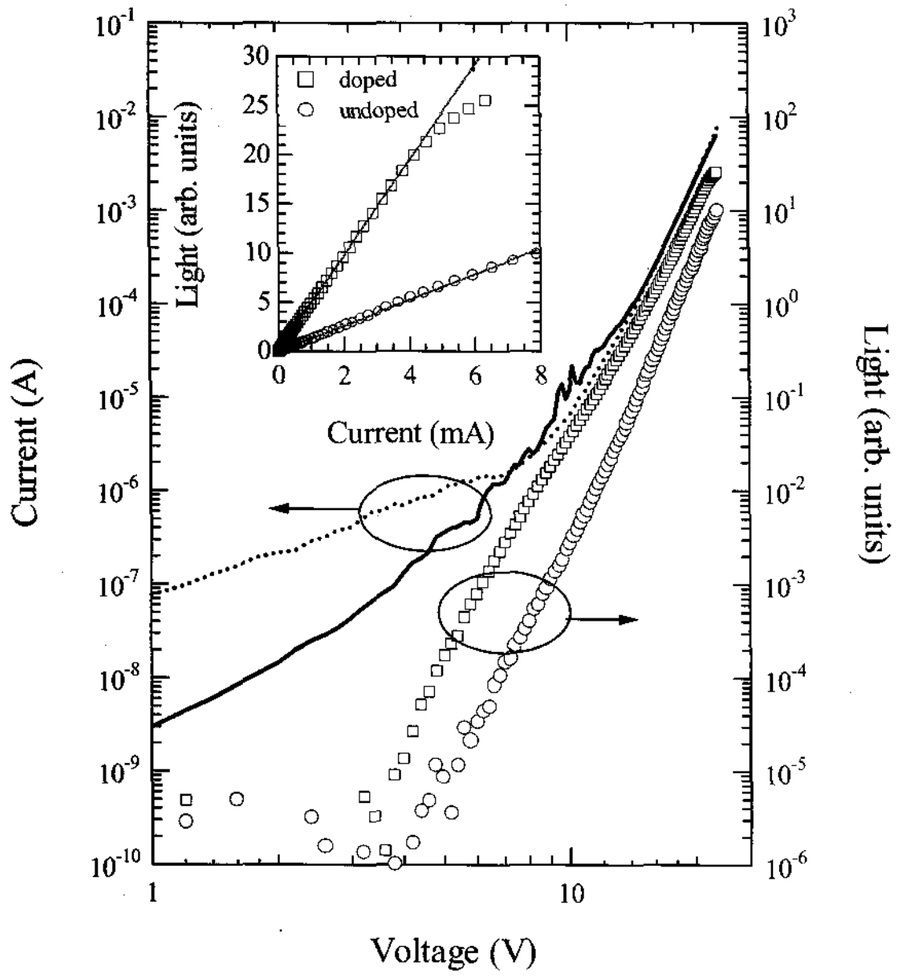


**Fig. 2.** The I-V-L characteristics of ITO/TPD (600 Å)/ $Alq_3$:DCM2 (2 %, 300 Å)/$Alq_3$ (300 Å)/Al and ITO/TPD (600 Å)/$Alq_3$ (600 Å)/Al devices. The inset compares the luminance-current (L-I) dependence of the two devices. The solid lines are the slopes of the L-I curves.

Fig. 3 shows the PL spectra of 2 % DCM2-doped $Alq_3$ thin film at various temperatures. The inset shows the temperature dependence of the PL intensity. The PL spectra show a peak around 515 nm caused by the radiative recombination of the singlet-excited state of $Alq_3$ and a strong peak at about 620 nm due to DCM2, indicating an efficient energy transfer from $Alq_3$ to DCM2. The PL intensity and the spectral shape are almost independent of temperature.

Fig. 4 shows the EL spectra of the ITO/ TPD/ $Alq_3$:DCM2 (2 %)/Al devices under a current density of 12.5 mA/cm$^2$ at various temperatures. The inset shows the temperature dependence of the EL intensities at 515 nm and 620 nm. Similar to PL, the EL spectra also show peaks around 515 nm ($Alq_3$) and 620 nm (DCM2). Although the PL intensity shows very weak temperature dependence, the EL peak at 620 nm from DCM2 increases with increasing temperature while the EL peak at 515 nm from the host $Alq_3$ decreases significantly above roughly 100 K. This difference indicates that direct charge carrier trapping at the dopant molecule plays an important role in addition to the energy transfer in the EL devices and that charge carrier trapping process is effective at high temperature.

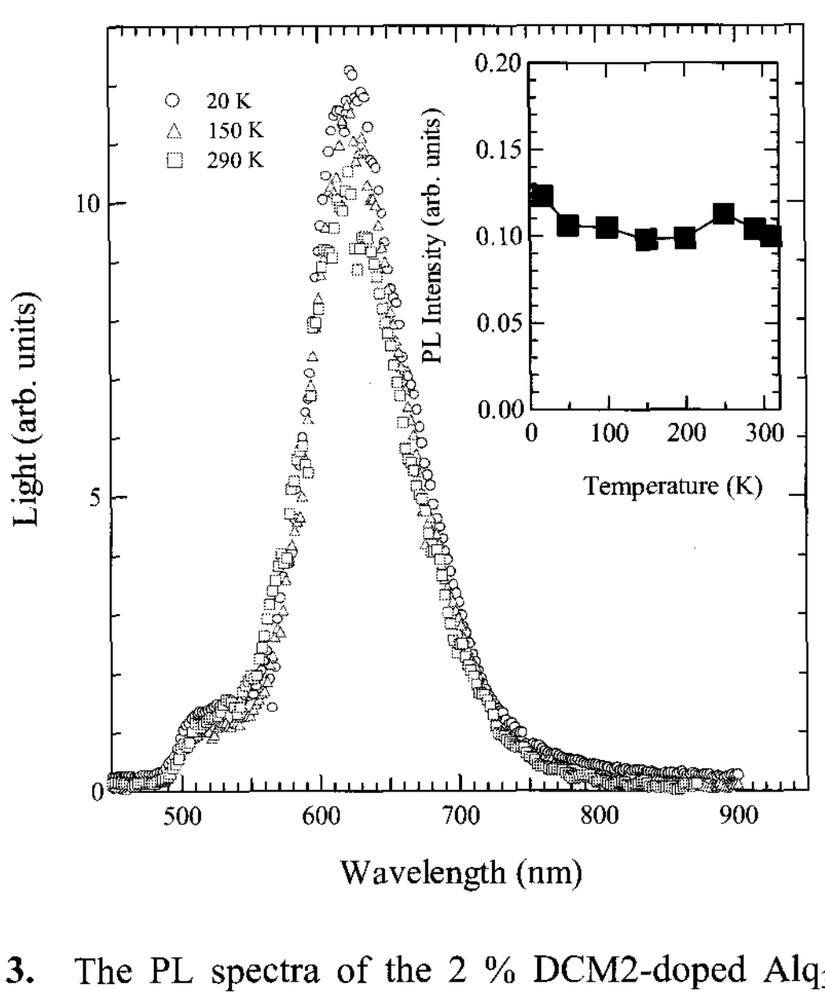


**Fig. 3.** The PL spectra of the 2 % DCM2-doped $Alq_3$ thin film at various temperature, 20 K (circle), 150 K (triangle), and 290 K (square). The inset shows the temperature dependence of the PL intensity.

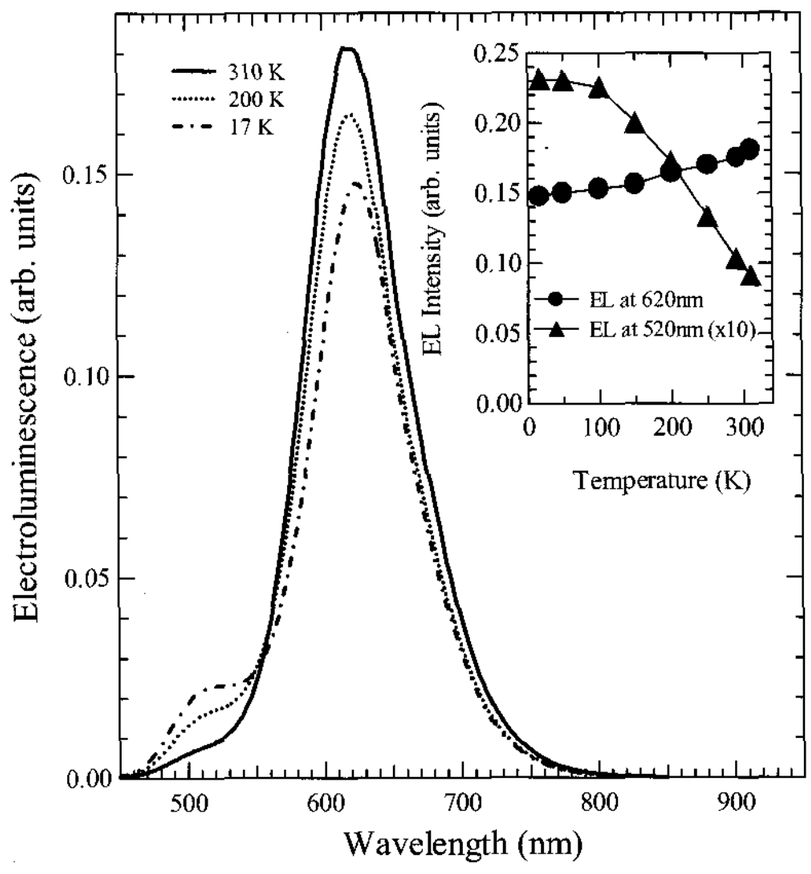


**Fig. 4.** The EL spectra of the ITO/TPD/$Alq_3$:DCM2 (2%)/Al devices under a current density of 12.5 mA/cm$^2$ at various temperatures. The inset shows the temperature dependence of the EL intensities at 515 nm and 620 nm.

Fig. 5 shows the L-I characteristics of the ITO/TPD/$Alq_3$:DCM2 (2 %)/Al devices. The EL intensity is superlinear with the current at low current densities, implying the injection-limited regime [10]. At high injection current densities, the EL emission from DCM2 shows a sublinear dependence on the current, $EL \propto I^{0.9}$ while the emission from $Alq_3$ shows a linear or slightly superlinear dependence, $EL \propto I^{1.1}$. We also observed that the PL intensity of DCM2 shows a sublinear dependence on the photoexcitation intensity. Therefore, the efficiency of the radiative recombination from DCM2 gradually decreases with the increase in either the current density or the photoexcitation intensity. The result implies that the exciton – exciton annihilation processes generally occur at high exciton densities.

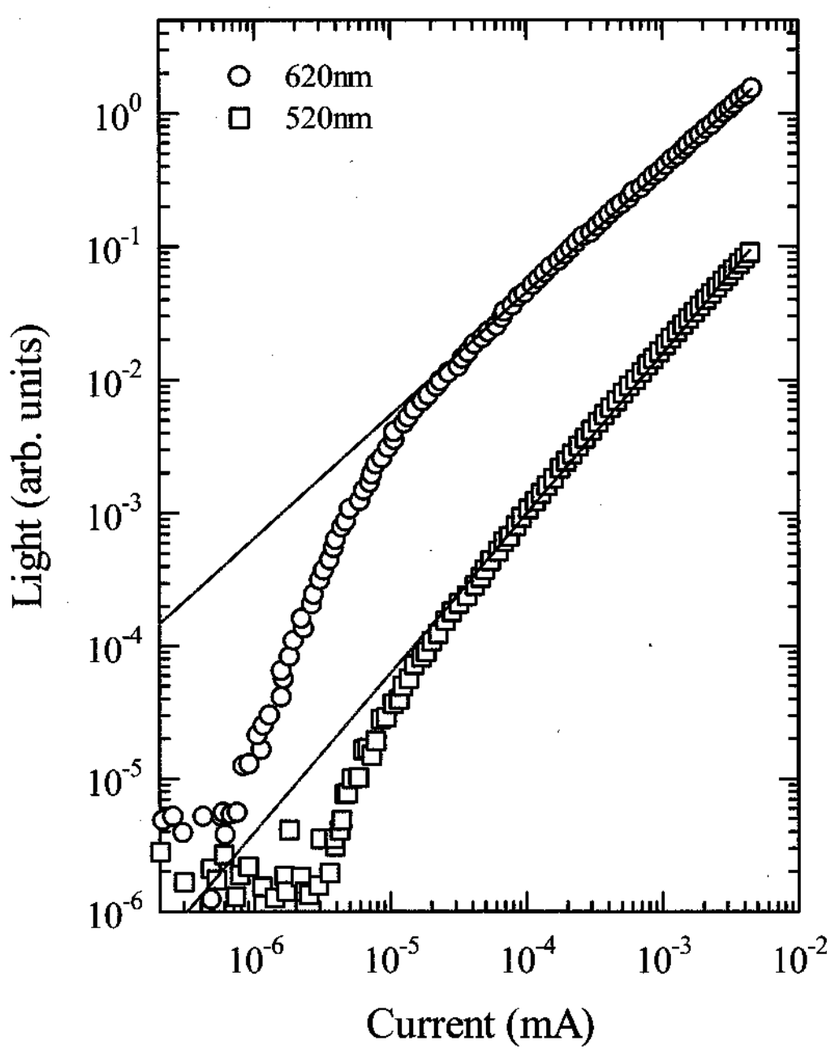


**Fig. 5.** The L-I characteristics of ITO/TPD/$Alq_3$:DCM2 (2 %)/Al. The solid lines are power-law fits ( $EL \propto I$ ) to the data at high currents.

Fig. 6 shows the schematic energy band diagram of ITO/TPD/$Alq_3$:DCM2 (2 %)/Al devices along with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of TPD, $Alq_3$, and DCM2. Due to the difference of the HOMO and LUMO energy levels between TPD and $Alq_3$, there are potential energy barriers at the TPD/$Alq_3$ interface that limit carrier injection and transport across the interface. Since the energetic difference between the HOMO levels of TPD and $Alq_3$ is low (~0.1 eV) compared with the LUMO differences (~0.5 eV), holes can relatively and easily surmount the barrier at high temperatures. Therefore, injected electrons and holes undergo recombination inside the $Alq_3$ layer near the TPD/$Alq_3$ interface. After an exciton is formed in $Alq_3$, energy transfer from $Alq_3$ to DCM2 occurs within the diffusion length of the exciton and/or the Förster energy transfer range. In addition, DCM2 can act as an efficient hole trap in $Alq_3$ since the HOMO level of DCM2 (5.4 eV) is lower that that of TPD (5.6 eV). Therefore, the increase of the EL emission efficiency from DCM2 with increasing temperature indicates that charge carrier trapping becomes efficient with increasing temperature.

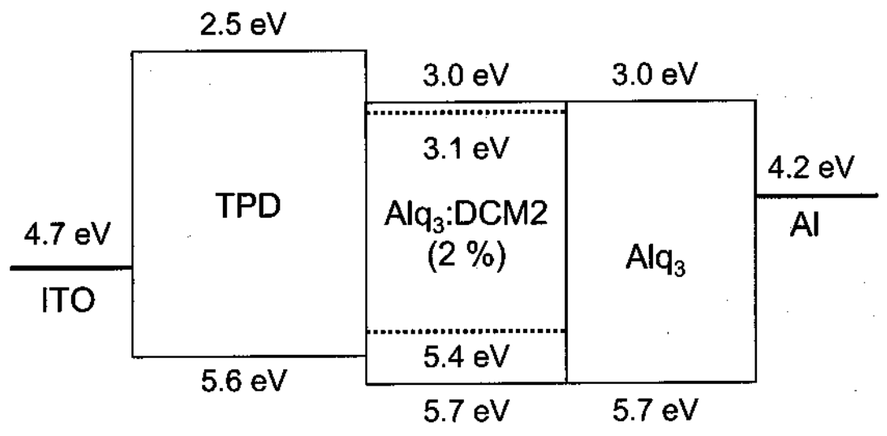


**Fig. 6.** The schematic energy band diagram of ITO/TPD/ $Alq_3$:DCM2 (2 %)/Al devices along with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of TPD, $Alq_3$, and DCM2.

## 4. Conclusions

We have studied the energy transfer and the charge carrier trapping processes in organic light-emitting diodes consisted of TPD as a hole-transporting layer, $Alq_3$ as the host, and DCM2 as the dopant. The emission from DCM2 is much stronger compared with the emission from $Alq_3$, indicative of efficient energy transfer from $Alq_3$ to DCM2. In addition, the EL emission from DCM2 increases with increasing temperature while the emission from the host $Alq_3$ decreases. The result indicates that direct charge carrier trapping becomes efficient with increasing temperature. The EL emission from DCM2 shows a slightly sublinear dependence on the current density, implying the enhanced quenching of excitons at high current densities due to the exciton - exciton annihilation.

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