

Thin Film Electroluminescence of Poly(phenylquinoxaline) Doped with Organic compound

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ABSTRACT

Poly-phenylquinoxaline(PPQ) is used as the electroluminescent(EL) materials to fabricate the thin film electroluminescent devices by means of the spin coating method. Doped with 1,3,5-triphenyl-2-pyrazoline(TPL), the EL spectrum of the devices is shifted to the blue-green region with its peak located at 465nm. The incorporation of a hole-transporting layer poly-vinylcarbazole(PVK) will enhance the EL intensity. The quantum efficiency is estimated to be about 0.2%. The devices can be driven by either positive or negative bias even though the current-voltage curve possesses a rectifying property.

1. Introduction

The studies of conjugated polymer light-emitting diodes (LED) have attracted a great deal of attention due to their excellent properties, such as, easy to fabricate, very low cost, high efficiency, adjustable luminescence colour, and the ability of making large area display panel on either rigid or flexible substrates. Right now, the most popularly used conjugated polymers for LED are phenylenevinylene (PPV) and its derivatives^[1,2,3]. Although high efficiency electroluminescence (EL) has been demonstrated on PPV and PPV/CN-PPV based diodes, their longevity and stability are rather poor, which prevent the polymer LED to be of practical use. To solve this problem, it is necessary to investigate the exact mechanisms of luminescence and aging of PPV, or to explore some new kinds of light-emitting polymer materials. In this work, we report the visible light emission from poly-phenylquinoxiline (PPQ) for the first time. The electroluminescence at blue-green colour region with the luminous efficiency of about 0.11 (lumen/W) is achieved.

2. Experiment

PPQ is a kind of optical nonlinear materials and possesses good heat-resisting and radiation-resisting properties, which would be benefited in improving the stability of the luminescence behavior. It could be doped by other organic materials, such as the triphenyl-2-pyrazoline (TPL) compound. Figure 1 shows the molecular structures of

PPQ and TPL. In this work, three kinds of EL devices were fabricated using PPQ as emitter materials:

(1) Glass/ITO/PPQ/Al, (2) Glass/ITO/PPQ/PVK/Al, (3) Glass/ITO/PPQ+TPL/PVK/Al. The PPQ thin film or the doped (with TPL) PPQ thin film was formed by spin coating method on an indium-tin oxide (ITO) coated glass substrate using a solution of PPQ in chloroform or a solution with appropriate weight ratios of PPQ and TPL in chloroform. Polyvinylcarbazole(PVK) thin film as a hole-transport layer was deposited in the same way using a solution of PVK in tetrahydrofuran. The thicknesses of PPQ and PVK are approximately 200nm and 150nm, respectively. After deposition, the sample was heated in vacuum(2×10^{-5} Torr) to 280°C for 4 hours in order to make the thin films strong and tough. Finally, an Al electrode was evaporated on the top of the film. To measure the photoluminescence(PL) spectra, the same films were also prepared on glass substrates without ITO and Al electrodes.

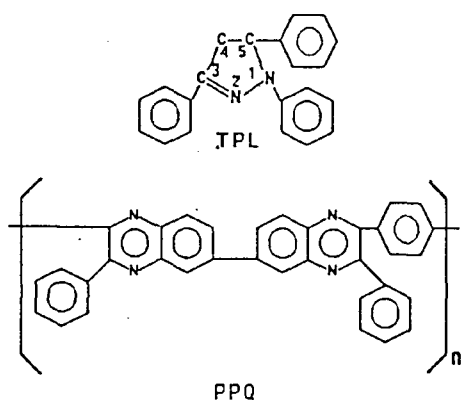


Fig.1 Molecular structures of triphenyl-2-pyrazoline(TPL) and poly (phenylquinoxaline) (PPQ)

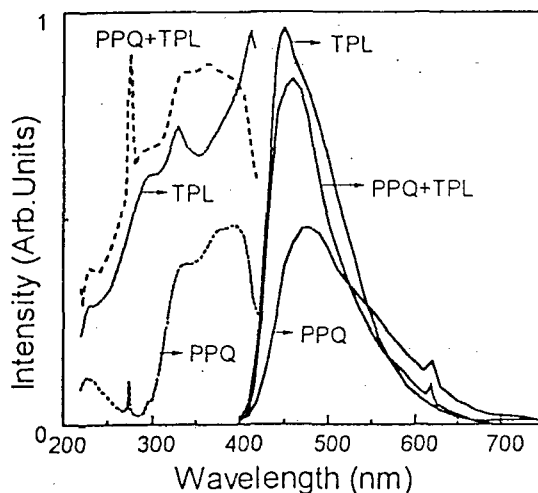


Fig.2 PLE (dashed curves) and PL (solid curves) spectra of TPL, undoped PPQ thin film, and doped PPQ thin film.

The PL and photoluminescence excitation (PLE) spectra of thin films were measured using a Hitachi 4010 fluorescence spectrometer. The excitation source was a Xe lamp with the 385 nm line used for PL measurements. The PLE spectra were measured in the wavelength range of 220-430 nm. The wavelengths of PL peaks of the samples were chosen as the monitor wavelengths. The EL spectra of these devices were measured by a Spex Fluorolog 212 spectrometer. The measurements of the electric properties were performed by routine instruments.

3. Results and discussion

Figure 2 shows the PL (solid curves) and PLE (dashed curves) spectra of TPL, undoped PPQ thin film, and doped PPQ (with TPL) thin film. The PL spectrum of TPL

is an asymmetric band with a peak at the wavelength of 448nm and a shoulder at 490nm. The full width at half maximum (FWHM) is about 90nm. The PL spectrum of PPQ is a broad band peaked at 468nm with a FWHM of 120nm. There is a small sharp peak at 619nm superposed on the long wavelength tail of the main peak. The origin of this peak is unknown. The PL spectrum of doped PPQ is almost the superposition of the PL spectra of PPQ and TPL. The peak is located at 458nm, while its FWHM is 80nm, i.e. smaller than the FWHMs of the peaks of TPL and PPQ. Again the sharp peak appears at the long wavelength tail. The PLE spectra of these three samples are quite different, but their long wavelength absorption thresholds are about the same (410nm), which implies that the energy band gaps of these three samples are almost the same. The PLE spectrum of doped PPQ (PPQ+TPL) layer is similar to that of undoped PPQ layer in the long wavelength range and to that of TPL layer in the short wavelength range. The PL spectrum of PVK thin film was also measured but is not shown here. The basic feature is a peak positioned at 420nm with a FWHM of 75nm, in coincidence with previous report^[4]. The PL and PLE measurements illustrate that the TPL is really doped in the PPQ film and the fundamental luminescence band of PPQ (undoped or doped) is located in the blue color region, and PVK has the energy gap larger than that of PPQ, so it could be used as a hole-transport layer in the PPQ/PVK heterostructure.

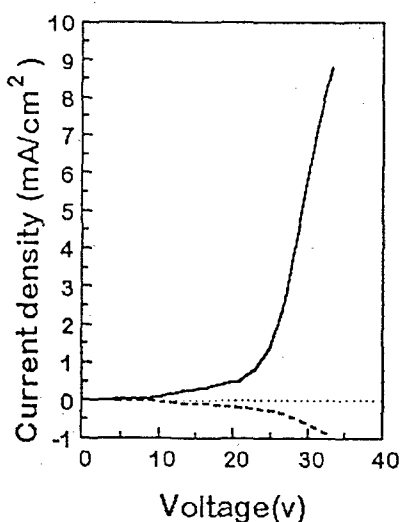


Fig.3 I-V curve of a PPQ/PVK EL device, ITO electrode applied with positive (solid) and negative (dashed) bias voltages.

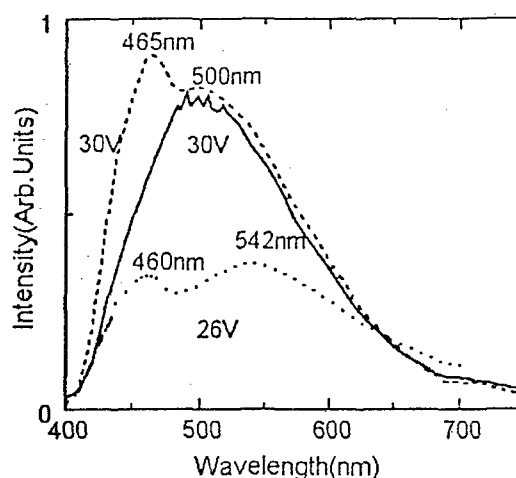


Fig.4 EL spectra of the undoped PPQ and the doped PPQ thin film devices. dotted curve: PPQ single layer device; solid curve: PPQ/PVK double-layer device; dashed curve:PPQ+TPL/PVK double-layer device

The electroluminescence was achieved for the samples under either positive or negative bias voltage. It was found that when the ITO electrode was biased to negative, the EL seems more stable than that operated under the positive bias voltage. The I-V characteristic of the sample shows rectifying-like behaviour. Figure 3 is a typical I-V curve of sample (2), the ITO/PPQ/PVK/Al device. Below the applied voltage of 20V,

the forward current and the reverse current are almost the same, while the EL is very weak that it is almost invisible in dark by the naked eye. The EL intensity increases as the bias voltage or the current increases. Similar I-V behaviours have been observed for samples (1) and (3). It could be seen that although the operation voltage is relatively high (25-35V), the driving current density is only about 0.2-0.6 mA/cm². So the power dissipation is relatively low, i.e. in the range of 15mW/cm², which seems to be a consequence of the high resistivity in the PPQ layer.

Figure 4 shows the EL spectra of three samples under the negative bias voltages. The EL emissions are basically in the wavelength range of blue-green, especially for sample (3), where the incorporation of TPL dopant dominates the EL peaks at the wavelength around 465nm and 500nm. In other word, the two peaks is exactly located at 448nm and 519nm after decomposing the EL spectrum for sample (3). The EL intensities of samples (2) and (3), both have been incorporated with a hole-transport layer PVK, are larger than that of sample (1) without the PVK layer by a factor of about two. It means that the insert of PVK layer prevents the emission quenching near electrode^[5], and keeps two kinds of injecting carriers equilibrium as well. The brightness of samples (2) and (3) is measured to be 5.5cd/m² at the current density of 0.5 mA/cm² and driving voltage of 30V. The luminous efficiencies are estimated to be 0.11 lumen/W for samples (2) and (3), and the quantum efficiencies are about 0.2%. Although this value is relatively low as compared with the quantum efficiency reported for poly(phenylene vinylene) (PPV)^[3], it would be improved further by optimizing the device structure. Nowadays, the quantum efficiency of PPV is about 0.75%, but for the first TFEL device using PPV as the emitting material^[1], it was only 0.05%.

In conclusion, it has been demonstrated that PPQ, which has been used as the insulating and nonlinear optical materials, could be an effective emitter used in a polymer electroluminescence device. Doped with TPL, a blue shift of the EL peak to the blue-green region is observed. The incorporation of a hole transport layer PVK will enhance the EL intensity. The EL device could be driven by either positive or negative bias voltage or even by an a. c. voltage with relatively low power dissipation. Thus the longevity of EL is expected. The quantum efficiency is estimated to be 0.2% and could be improved further by optimizing the layer thicknesses and uniformity. But the luminescence mechanism of the device is not known exactly yet.

References

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