An electroluminescent device made with a new fluorescent dye containing 1,3,4-oxadiazole

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Herein, we report an investigation on the use of a new derivative of 1,8-naphthalimide containing 1,3,4-oxadiazole for the fabrication of organic light emitting diodes. The 1,3,4-oxadiazole moiety facilitates the injection of electrons from the cathode of aluminium, and the 1,8-naphthalimide moiety acts as an emitting centre. Green–yellow electroluminescence peaking at 532 nm, which can reach a luminance of 225 cd m^{-2} at an applied voltage of 27 V, was observed. The maximum luminous efficiency is 0.43 lm W^{-1} at 19 V.

In recent years, organic light emitting diodes (LEDs) have intrigued many researchers owing to their potential for applications in display technology. Currently, there are two candidates for the active layers in organic LEDs, molecular fluorescent dyes and conjugated polymers. Molecular dyes are relatively more easy to purify, but liable to suffer from recrystallization due to Joule heat (Joule heat Q is the heat produced when the device operates; $Q=I^2Rt$). By contrast, conjugated polymers are believed to be more stable and easily fabricated into LED devices. However, they are relatively difficult to purify. This is a disadvantage because the purity of the materials is extremely crucial to the performance of LEDs.

It is well known that to achieve good performance in LEDs, injection of electrons and holes should be balanced. This requires that the energy level of the active layer materials matches the work function Φ of the electrodes and for most organic materials, ITO-coated glass can provide good hole injection when used as an anode contact. In order to facilitate injection of electrons, the metal used as the cathode should have a low value of Φ. For example, Ca and Mg, which have low Φ, can provide relatively good electron injection; however they are too reactive and cause problems in the stability of the device. Hence, aluminium, which has a relatively high workfunction yet is fairly stable towards air and moisture, is often used as the cathode contact. Therefore, it is desirable to prepare emissive materials with high electron affinity which matches the work function of more stable metals such as aluminium.

The electron-withdrawing oxadiazole unit is believed to have high electron affinity and should facilitate electron injection. Several small organic molecules, such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), have been successfully used as electron-injection materials to improve the balance of charge injection and to increase the photon/electron quantum efficiency.[1–4] The improved performance is believed to result from the high electron affinity of the oxadiazole unit in the molecules. Recently, several analogues of PBD have been synthesized and shown to be good electron injection materials.[5] On the other hand, polymers containing oxadiazole also attract much attention because of the advantages of polymers over small molecules.[6,7] Meier *et al.*[8] improved the quantum efficiency of LEDs based on polymers either containing an oxadiazole ring in the main chain or with oxadiazole side-groups. Such polymers containing the electron-withdrawing oxadiazole units facilitate electron injection.

Here, we investigate a new fluorescent dye containing 1,3,4-oxadiazole (2-phenyl-5-{4[2-(6-dimethylamino-2*H*-benz[*d,e*]isoquinoline-1,3(2*H*)-dione-2-yl)propyl]amino}phenyl-1,3,4-oxadiazole, NIO) for the fabrication of organic LEDs. NIO was synthesized according to a modified literature method.[9,10] The synthesis and characterization of this compound have been reported elsewhere.[11] Fig. 1 shows the structure of the NIO molecule and the fabricated device.

Experimental

Substrates used were ITO-coated glass slides with a sheet resistance of <100 Ω □$^{-1}$. The ITO-coated glass was etched, patterned and carefully cleaned to serve as the anode. Metal-free phthalocyanine (H_2Pc) (for type II devices) was vacuum evaporated onto the ITO substrates at pressures below 2×10^{-3} Pa. After the phthalocyanine has been fabricated (for type II devices), poly(vinyl carbazole) (PVK) was spin-cast onto the substrates at 2500 rpm from a 1,2-dichloroethane solution at a concentration of 4 mg ml^{-1}. H_2Pc is insoluble in 1,2-dichloroethane, which guarantees a good interface of H_2Pc/PVK after the PVK layer was fabricated. Then, a layer of NIO was vacuum evaporated at a pressure below 2×10^{-3} Pa. Finally, metal contacts of aluminium were vacuum evaporated at the same pressure. For each substrate, a metallic mask was used to yield four samples with active areas of *ca.* 14 mm^2.

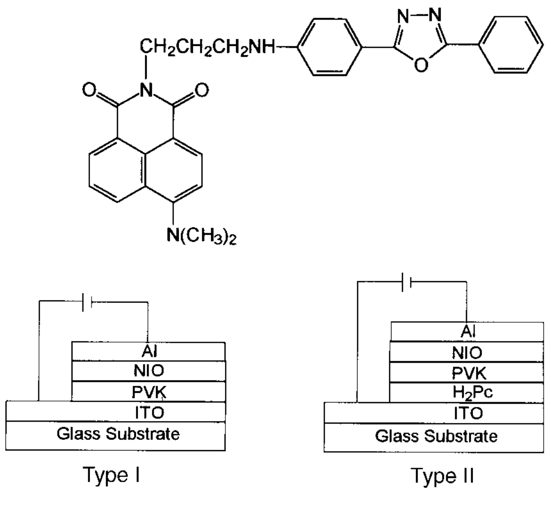


Fig. 1 Structure of the molecule and fabricated devices

Absorption spectra were measured on a Hewlett Packard 8452A Diode Array spectrophotometer. Electroluminescent (EL) spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer with a high-quality optical fibre gathering and transferring the EL emission to the detecting system. Current density–voltage (*J–V*) characteristics were obtained using a programmable Solartron 7081 Precision Digital Voltmeter interfaced to a personal computer through an IEEE 488 interface board. The luminances were measured with a LS-1 portable luminance meter. All measurements were performed at room temperature in air.

Results and Discussion

Fig. 2 shows the *J–V* characteristics for the fabricated devices. As can be seen, the current density *J* in the type II device is much higher than that in the type I device under the same forward bias, although both increase superlinearly with increase in voltage. This means that the layer of H_2Pc greatly facilitates the injection of holes from the anode of ITO. This result is in good agreement with previous work,[12] in which we improved the stability of the device and elevated the current level in the device by inserting a layer of H_2Pc between ITO and PVK.

Fig. 3 illustrates the brightness *vs.* voltage characteristics for type I and II devices. The brightness also increases superlinearly upon increasing the voltage, just like the current density. However, beyond a given value, the brightness gradually decreases with further increase in voltage. This implies that when the device works under higher biased voltage, the Joule heat is more notable and results in the drop of the EL brightness and efficiency and we have proposed a tentative explanation of this phenomenon in ref. 12. It should be noted that although the current density in the type I device is lower than that in type II, the brightness of the type I device is higher than that of the type II device when the voltage is >20.5 V whilst being lower below 19.5 V. The maximum brightness of the type I and II devices is 225 cd m^{-2} at 27 V and 154 cd m^{-2} at 23.5 V, respectively. The maximum luminous efficiency calculated by $\eta_L = \pi B/JV$ is 0.43 lm W^{-1} (at an applied voltage of 19 V) and 0.043 lm W^{-1} (at a biased voltage of 15.5 V) for the type I and type II device, respectively. In other words, the efficiency of the type II device is an order of magnitude lower than that of the type I device. The major carriers in the type I device are probably holes, while insertion of the H_2Pc layer in the type II device improves the injection of holes further. Therefore, imbalance between hole injection and electron injection is aggravated, and results in a decline of the efficiency. On the other hand, because the turn-on voltage of LEDs is controlled by the major carrier,[13] the insertion of the H_2Pc layer lowers the turn-on voltage from 12 V (type I device) to 7.5 V (type II device).

Fig. 4 demonstrates the measured and normalized EL spectra for the type I device under different forward bias. The device has a broad luminescence spectrum which spans the range 475–650 nm with a peak at *ca.* 532 nm. The normalized spectra are basically identical indicating that the EL spectra do not change with the voltage and means that the emission zone stays within the NIO layer when the voltage is varied. Because the layer of NIO has a certain thickness, whether the emission zone shifts with the applied voltage or not is not clear. Even if the emission zone shifts, we can not observe it from the EL spectra until the emission zone moves out of the NIO layer and into another layer, thereby changing the EL spectra. Furthermore, when the emission zone shifts, it is most likely to shift towards the minor carrier side.[14] In this case, the minor carriers are electrons, and if the emission zone shifts, it will shift towards the cathode but still within the NIO layer. This makes it more difficult to determine whether the emission zone

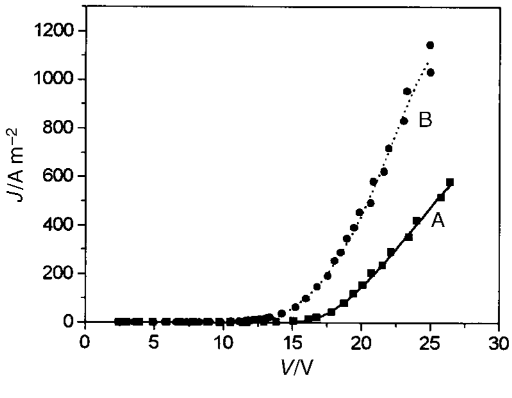


Fig. 2 Current density *vs.* voltage (*J–V*) characteristics of (A) type I and (B) type II devices

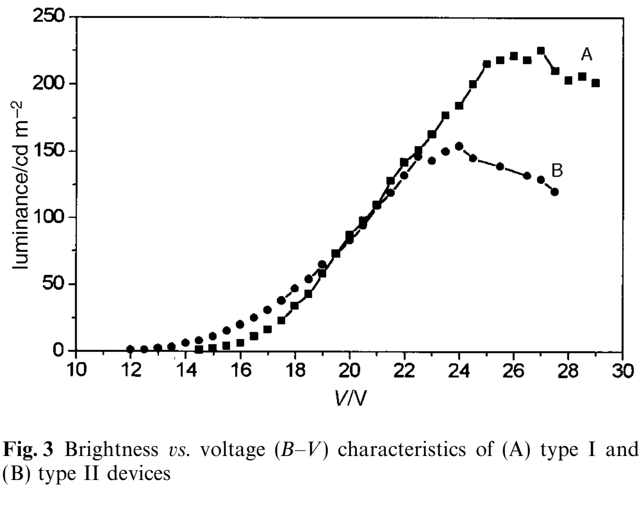


Fig. 3 Brightness *vs.* voltage (*B–V*) characteristics of (A) type I and (B) type II devices

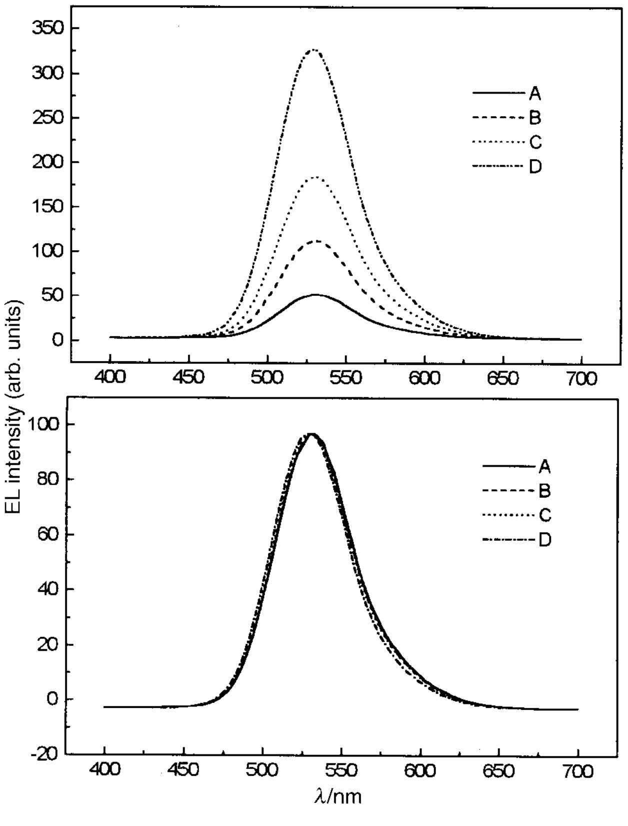
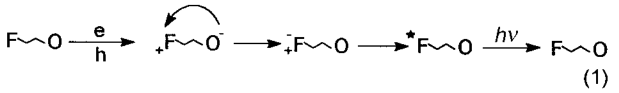


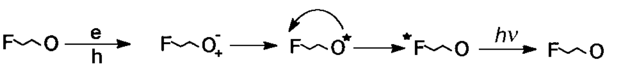
Fig. 4 Original (top) and normalized (bottom) EL spectra of a type I device under different forward bias. A: 18 V; B: 21 V; C: 24 V; D: 27 V.

shifts or not. In the type II device, the situation is the same and Fig. 5 shows the original and normalized EL spectra for the type II device. It can be seen that the emission of the type II device also arises from the NIO layer.

Fig. 6 shows the absorption spectra of NIO in $CHCl_3$ solution and in a thin solid film. The former shows two peaks at 332 and 420 nm while the latter shows two peaks at 340 and 432 nm. The two peaks correspond to the absorption of the oxadiazole moiety and the 1,8-naphthalimide moiety, respectively. In the EL spectra, however, there is only one peak at *ca.* 532 nm. Because the oxadiazole unit has a high electron affinity, it is possible that the electron is injected into the LUMO of the oxadiazole. Based on this evidence, we propose two possible mechanisms for the emission [eqn. (1) and (2)].



(1)



(2)

Here, F and O are the 1,8-naphthalimide and the 1,3,4-oxadiazole moiety, respectively (see Fig. 1), and e and h are the electron and hole, respectively. In the mechanism shown in eqn. (1), when the device is forward biased, electrons are injected from the Al cathode into the π^* orbital of the oxadiazole moiety and holes from the anode of ITO are injected into the π orbital of the 1,8-naphthalimide moiety. An intramolecular electron transfer thus occurs and the electrons are transferred to the π^* orbital of the 1,8-naphthalimide moiety. The holes and electrons then recombine in the 1,8-naphthalimide moiety to form excitons which then undergoes radiative decay. In the mechanism shown in eqn. (2), an intramolecular energy transfer is involved. When a voltage is applied to the device, both holes and electrons are injected from the corresponding electrodes into the π and π^* orbitals of the oxadiazole moiety where they recombine. Then, the energy of the excited oxadiazole moiety is transferred to the 1,8-naphthalimide moiety leading to electroluminescence. Therefore, only the characteristic emission of the 1,8-naphthalimide moiety is present in the EL spectra.

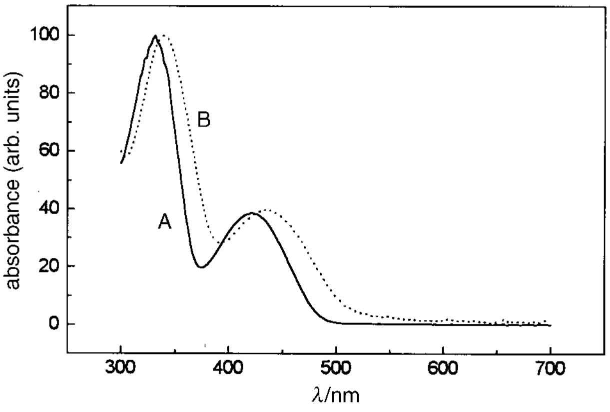


Fig. 6 Normalized absorption spectra of (A) NIO in $CHCl_3$ solution and (B) in thin solid film state

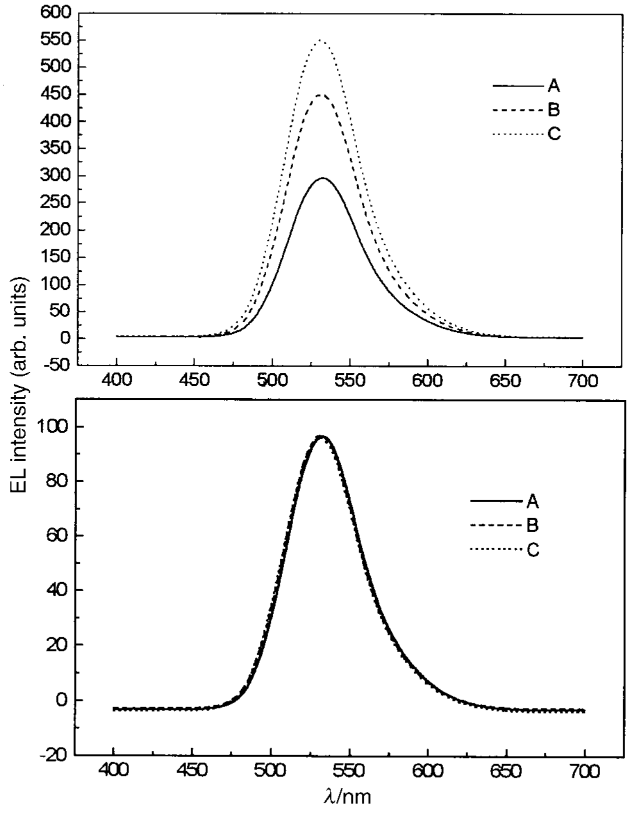


Fig. 5 Original (top) and normalized (bottom) EL spectra of a type II device under different forward bias. A: 16 V; B: 20 V; C: 24 V.

In order to compare the EL spectra of type I and II devices, we plotted the normalized absorption spectrum of thin solid H_2Pc film and EL spectra of type I and II devices in Fig. 7. It can be seen that the absorption spectrum of H_2Pc overlaps with the emission spectrum of NIO in the range 550–650 nm. However, the EL spectra of type I and II devices are essentially the same in spite of the overlap. In other words, when the emission of NIO comes out through the H_2Pc layer, almost no absorption by H_2Pc is observed. In ref. 12 we observed that the emission from the Alq_3 [tris(8-hydroxy)quinoline aluminium] layer in the ITO/H_2Pc/PVK/Alq_3/Al device was absorbed partially by the H_2Pc layer in the region where the absorption spectrum of H_2Pc overlaps with the emission spectrum of Alq_3. The reason for the difference in this case is, as yet, not clearly understood.

Conclusions

Organic LEDs based on a new derivative of 1,8-naphthalimide containing 1,3,4-oxadiazole have been fabricated. The 1,3,4-oxadiazole moiety facilitates the injection of electrons from the aluminium cathode and the 1,8-naphthalimide moiety acts as the emitting centre. Green–yellow electroluminescence, which can reach a luminance of 225 cd m^{-2} at an applied voltage of

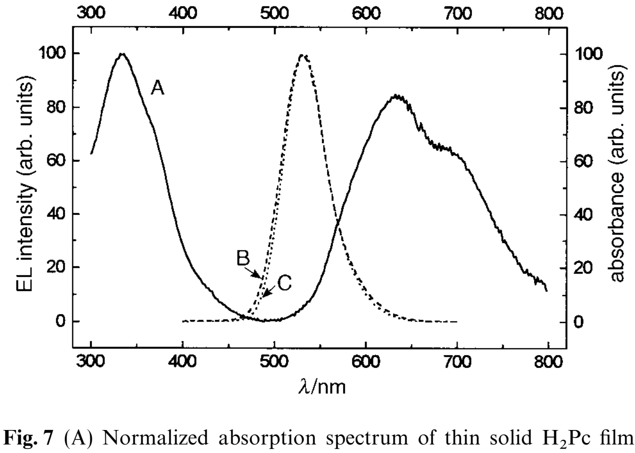


Fig. 7 (A) Normalized absorption spectrum of thin solid H_2Pc film, and EL spectra of (B) type I and (C) type II devices

27 V, was observed. The maximum luminous efficiency is 0.43 lm W^{-1} at 19 V.

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