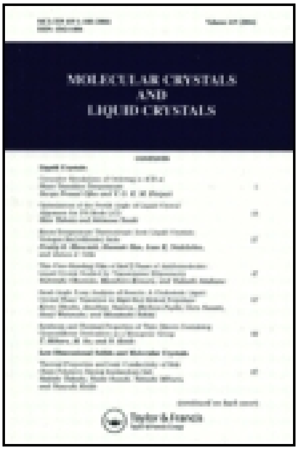

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Electroluminescence from Triplet Excited States of Benzophenone Derivatives

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ELECTROLUMINESCENCE FROM TRIPLET EXCITED STATES OF BENZOPHENONE DERIVATIVES

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Abstract This paper investigated electroluminescent (EL) characteristics of multilayer organic light emitting diodes (LEDs) utilizing poly(methylmethacrylate) films containing typical phosphorescent benzophenone (BP) derivatives such as BP or 4,4'-dichlorobenzophenone as an emitting layer. The EL spectra exhibit agree well with the phosphorescence spectra of emitting materials at a low temperature. Combined analysis of temperature dependence of EL intensity, EL spectra, and EL decay time indicate that the EL of these LEDs originates from the triplet excited states of the BP derivatives.

INTRODUCTION

In organic light emitting diodes (LEDs), electroluminescent (EL) properties such as colors and quantum efficiencies are influenced by the excited state properties of their emitting materials as well as their device structures. For organic molecules used as emitting materials in organic LEDs, statistical production of both the singlet and triplet excited states of the molecules is expected to occur via charge recombination because there is no spin selectivity in the recombination process. This means that EL can be observed from triplet excited states if an appropriate phosphorescent molecule is used as an emitting material. However, to date there has been only a preliminary study on the EL originating from triplet excited state molecules.[1] Recently, we have reported the observation of EL from triplet excited state molecules in multilayer organic LEDs consisting of a hole transporting, an emitting, and an electron transporting layer. Benzophenone (BP) derivatives are used as emitting materials because they are typical phosphorescent molecules and their phosphorescent behavior has been well characterized.[2]

EXPERIMENT

Figure 1 shows the structure of multilayer LEDs and the chemical structures of organic materials. The multilayer LEDs, consisting of poly(methylphenylsilane) (PMPS) as a hole transporting layer, poly(methylmethacrylate) (PMMA) containing 10 wt % of BP or 4,4'-dichlorobenzophenone (CBP) (BP or CBP:PMMA) as an emitting layer, and 2-(4'-t-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxadiazole (PBD) as an electron transporting layer, respectively, were prepared on indium-tin-oxide (ITO) coated glass substrates. Each organic layer was 50 nm thick. An Al cathode was vacuum vapor deposited on top of the PBD layer. The fabrication procedure has been described in detail elsewhere.[3] Current-voltage-EL intensity (I-V-EL) characteristics, EL spectra, and EL decay time were measured in accordance with the previously reported methods.[3,4]

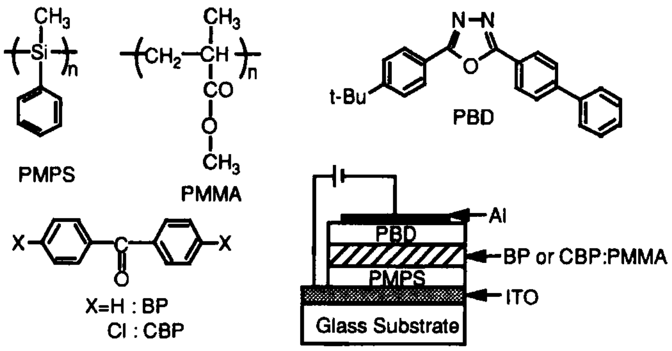

FIGURE 1 Structure of LEDs and chemical structure of materials.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the I-V-EL curves of an LED with a BP:PMMA layer. The current, which like other PMPS-based LEDs, is dominated by holes,[4] is larger at 273 K than at 100 K for the same applied voltages, suggesting that hole injection from the ITO electrode and

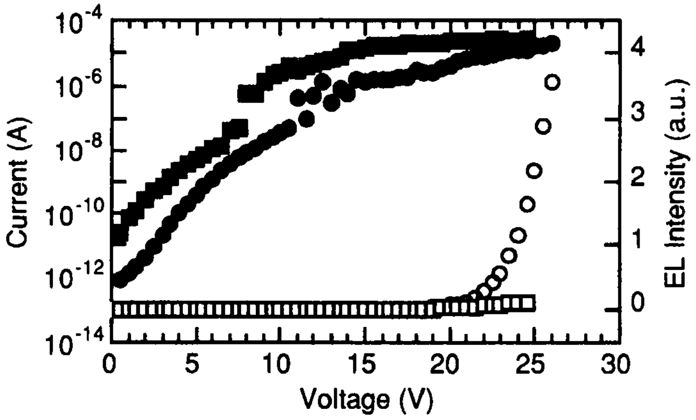

FIGURE 2. Temperature dependence of I-V-EL curves of an LED with a BP:PMMA emitting layer. The symbols represent current and EL intensity at 273 K (■,□), and those at 100 K (●,O), respectively.

hole transport occur efficiently at higher temperatures. An increase in EL intensity is observed only at 100 K, indicating that the EL from the LED is more efficient at 100 K than at 273 K. At 24 V, there is a more than ten-fold difference in the EL intensity at the two temperatures. The temperature dependences of the EL intensity are similar to those of the phosphorescence intensity of the BP derivatives. The phosphorescence emission from the BP derivatives was clearly observed at 100 K but it could hardly be detected at 273 K.

The emissive species of these LEDs were directly confirmed from their EL spectra. Figure 3 (a) shows the EL spectrum of an LED with a BP:PMMA layer together with the photoluminescence (PL) spectrum of BP:PMMA at 100 K. The three peaks around 420, 450, and 480 nm observed in the PL spectrum correspond to the vibrational structure of BP phosphorescence.[2] The EL spectrum is almost identical to the phosphorescence spectrum of BP:PMMA, suggesting that the EL arises from the triplet excited states of BP.

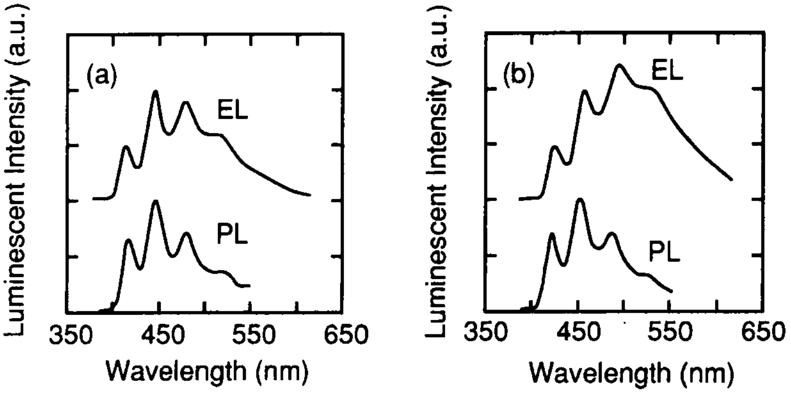

FIGURE 3 EL spectrum of an LED with a BP:PMMA layer and PL spectrum of BP:PMMA (a), EL spectrum of an LED with a CBP:PMMA layer and PL spectrum of CBP:PMMA (b), at 100 K.

For LEDs with a CBP:PMMA layer, the EL spectrum is composed of the phosphorescence of CBP (higher energy side) and an additional emission (lower energy side), whose origin is unknown at the present stage (see Fig. 3(b)). However, this EL spectrum indicates that the triplet excited states of CBP, generated by the electron-hole recombinations are partly responsible for the EL. The additional emission may originate from an exciplex generated at the PBD/CBP:PMMA interface.

In general, the triplet excited states of organic molecules have a longer lifetime than the singlet excited states because the electronic transition from the former to the latter is a spin forbidden process. In order to further confirm the emissive species of the EL, we measured the EL decay time of the LED with a BP:PMMA layer. Figure 4 shows the EL decay profile of the LED when it was operated with a 400 ns rectangular pulse voltage (35 V) at 100 K. The decay profile is well fitted to a single exponential function with a decay time of 46.8 μs. The fact that the observed decay time was longer than the ordinary fluorescence lifetime (~10 ns) strongly suggests that the EL arises from the triplet excited states of BP.

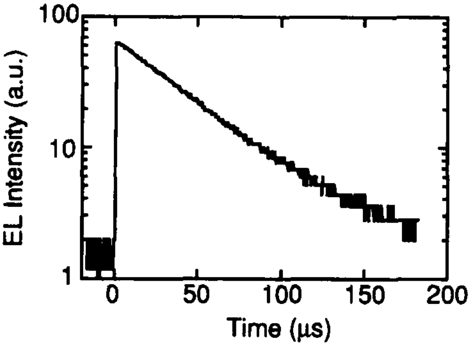

FIGURE 4 EL decay profile of the LED with a BP:PMMA layer at 100 K.

CONCLUSIONS

We have investigated the EL characteristics of multilayer LEDs in which PMMA films containing BP or CBP were used as the emitting layer. The EL intensity of these LEDs exhibits a marked temperature dependence; when the LED with a BP:PMMA layer was operated at 24 V, the EL intensity at 100 K was more than 10 times that at 273 K. The three characteristic peaks of the phosphorescence spectrum of BP or CBP were observed also in the EL spectrum of LEDs with either BP or CBP :PMMA layer. In particular, the EL spectrum of LED with a BP:PMMA layer is almost identical to the phosphorescence spectrum of BP. The EL showed a rather slower decay time of 46.8 μs. All these results indicate that the EL of these LEDs originates from triplet excited states of these BP derivatives. Triplet excited states can be generated in organic LEDs via two processes; one is direct generation by charge recombination, and the other is indirect generation through intersystem crossing from the singlet excited states. Further studies are currently in progress to determine the contribution of the triplet excited states generated by the former process.

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