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NARROW BANDWIDTH BRIGHT SCARLET ORGANIC ELECTROLUMINESCENT DEVICE BASED ON N,N'-BIS[4-(N,N-DIMETHYLAMONO)-BENZYLIDENE]-DIAMINOMALEONITRILE DYE

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

A novel red dye, N, N'-bis[4-(N,N-dimethylamino)-benzylidene]diaminomaleonitrile (BAM), was prepared by reacting diaminomaleonitrile with 4-(N,N-dimethylamino)-benzaldehyde and were characterized by ^{1}H NMR, UV absorption and photoluminescence. The BAM dye showed an absorption peak wavelength of 530 nm and bright photoluminescence with a peak wavelength at 675 nm. It was used as the doped emitter for fabricating a bright scarlet organic electroluminescent (EL) device. The structure of the double-layer EL device consisted of a hole-transport layer and a luminescent layer between ITO glass and magnesium electrodes. The hole-transport layer was a poly(N-vinylcarbazole) (PVK) film. The luminescent layer consisted of a host material, 8-hydroxyquinoline aluminum (Alq$_3$), and BAM dye as the dopant. A bright light with the peak of 620 nm and narrow bandwidth of 50 nm was obtained in the device with a maximum luminance of 6230 cd/m^2. The emis-

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sion spectra almost unchanged as the luminance increased with increasing injection current and the bias voltage. A tentative explanation from both the electronic distribution viewpoint and the molecular geometric analysis for the narrow bandwidth of this red dye was offered.

Key Words: EL device; Red light; Dye; Doping film; Electroluminescence

INTRODUCTION

Organic electroluminescent (EL) devices based on low molecular weight materials and polymers have attracted a great deal of attention in the fabrication of full color flat-panel displays due to their high brightness, low driving voltage and ease of processing [1-3]. Since Tang and VanSlyke [1] reported the first high efficiency double-layer organic EL devices in 1987, many researchers have fabricated high performance green organic EL devices using 8-hydroxyquinoline aluminum (Alq_3) [4]. Additionally, bright blue organic devices using certain complexes and distyryl derivatives [5-8], and red and orange organic EL devices using Eu or Ru complexes and DCMs organic laser dyes [9-12] have also been reported. Moreover, red organic EL devices with high brightness have been fabricated using complicated doping systems and DCM2 dye as the emitter [13]. However, like any other new fields, a number of technological challenges need further attention for the development of viable organic EL device, such as lengthening device lifetime and fabricating bright saturated monochromatic light emission EL devices. Typically, the broad EL spectrum of organic EL devices leads to unsaturated emission colors which can be narrowed using absorption filter [14] or microcavity [15]; theses methods can result in a reduction of the efficiency or a strong angular dependence of the color. Therefore, it is essential to develop a saturated color emission organic EL device without the using of such filters, which has proven to be particularly difficult. Meanwhile, it is well known that the full-width at half-maximum (FWHM) of DCMs, which included DCM1 and DCM2 (Figure 1) [12], now popularly used for red light EL device is more than 100 nm, which is not monochromatic for practical application in a display without the use of filters. Therefore, the development of saturated red emitters with narrow FWHM is demanded.

Herein, we report on the synthesis of novel red organic dye, N,N’-bis[4-(N, N-dimethylamino)-benzylidene] diaminomaleonitrile (BAM) for the fabrication of novel saturated bright scarlet EL device with a narrow FWHM.

EXPERIMENTAL

Materials

Diaminomaleonitrile with 4-(N,N-dimethylamino)-benzaldehyde were purchased from the Tokyo Kasei (TCI), and were used as received. Other reagents were purchased from KANTO and were used without further purification.

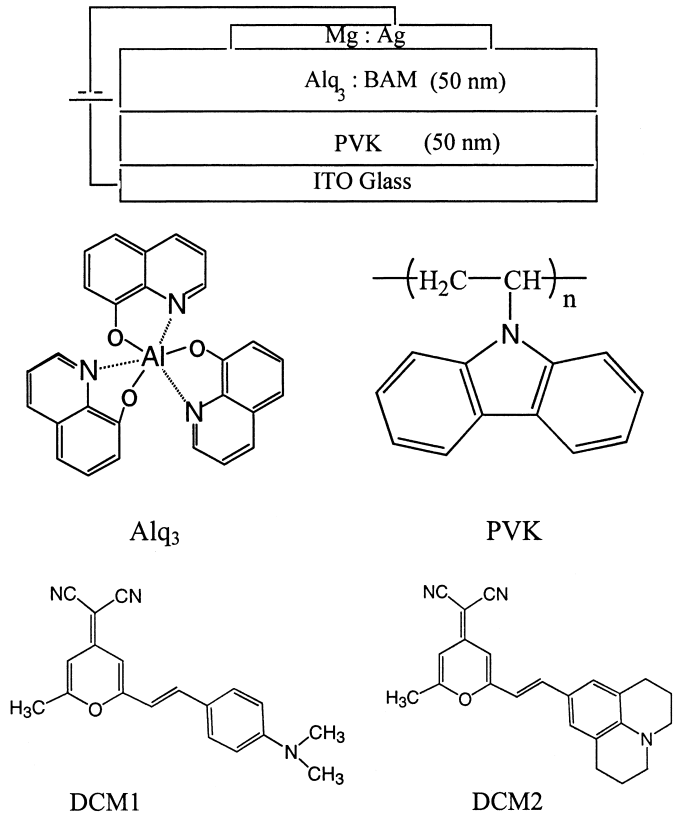
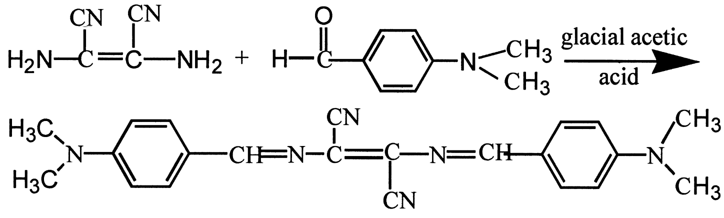


Figure 1. The structure of the EL device and the materials used and in this study.

Synthesis of the BAM Dye

A 100 mL three-necked, round-bottomed flask fitted with a magnetic stirrer was charged with 5.96 g (40 mmol) of 4-(N,N-dimethylamino)-benzaldehyde, 2.16 g (20 mmol) of diaminomaleonitrile, 60 mL of acetic acid under a nitrogen atmosphere. The resulting mixture was refluxed at about 120°C for six hours. The color of the mixture changed from blond to dark red after the reaction. After cooling, the product precipitated from solution (Scheme 1). The precipitate was puri-



Scheme 1.

fied by flash silica gel column chromatography (chloroform/methanol: 20/1) and was sublimated under reduced low pressure (2×10^{-5} torr) to afford a metallic luster solid in 76% yield. ^{1}H NMR ($CDCl_3$, ppm) 8.51 (2H, s, C-H), 7.79 (2H, s, Ar-H), 6.65 (2H, s, Ar-H), 3.04 (12H, s, CH_3). Anal. Calcd. For $C_{22}H_{22}N_6$: C, 71.35; H, 5.95; N, 22.70. Found: C, 71.32; H, 6.02; N, 22.85. MS (EI) m/e: 370.

Measurements

UV spectrum was recorded using a JACSO V-570 UV-VIS spectrophotometer with a evaporated film on a quartz substrate. The photoluminescence spectrum (PL) of the organic film was measured in air using a JASCO FP-777 spectrofluorometer. EL spectrum was measured on the same apparatus by blocking the xenon excitation lamp and scanning the emission from the cell.

EL device was fabricated on an ITO-coated glass substrate with a sheet resistance of 20 Ω/sq, which was ultrasonically cleaned successively by detergent solution, followed by deionized water, isopropanol, and methanol, and dried by N_2 gas. PVK polymer was used as the hole transport material, and its film (50 nm) was formed by spin casting from the 1,2-dichloroethnane solution (12 g/L) for 30 seconds. Alq_3 and BAM (100:1 molar ratio, 50 nm thick) were coated onto the polymer film by vacuum co-evaporation method from two separate sources. The Mg:Ag (10: 1) alloy cathode was thermally evaporated at a pressure of 2×10^{-5} Torr. The electrode area of the EL device was 12 mm^2. The structure of the EL device and the materials used in this study are shown in Figure 1.

RESULTS AND DISCUSSION

UV Spectrum and PL Spectrum of the Films

Figure 2 shows the absorption, photoluminescence (PL) spectra of BAM dye. In the same figure, the PL spectrum of the Alq_3-BAM co-evaporated film is also included. The absorption peak wavelength of BAM is 530 nm, corresponding to the emission peak of the host material Alq_3, which makes BAM a very suitable dopant for Alq_3-based organic EL devices. The PL spectrum of BAM shows that emission lies in the red region with a peak at 675 nm. As for the BAM-doped, Alq_3 co-evaporated film, the PL peak wavelength is blue shifted to 620 nm due to the formation of an exciplex between the Alq_3 and BAM molecules, which is almost as same as that in the DCM-Alq_3 doping system [12].

The EL Spectra of the EL Device

The EL spectra of the double layer device at various drive voltages are shown in Figure 3. An emission maximum at 620 nm was clearly visible as a

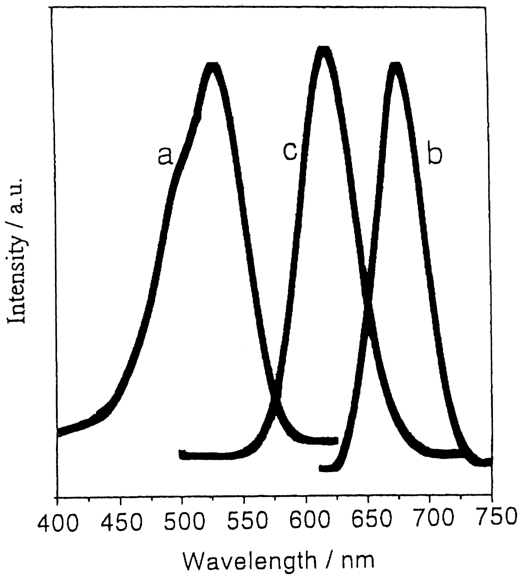


Figure 2. (a) UV-Vis absorption of BAM film; (b) PL spectra of BAM film; (c) BAM (1 mol%) Alq_3 co-evaporated film on quartz substrate.

bright scarlet emission in a lighted circumstance. The organic EL device emits saturated scarlet color, and there is no peak of Alq_3 at about 530 nm, which indicates that energy is effectively transferred from Alq_3 to BAM in the co-evaporated film. The emission spectra remained nearly constant as the luminance increased with increasing injection current and bias voltage, although the emission intensity of Alq_3 increased with increasing bias voltage in the doping system [13]. Furthermore, from the photograph of the organic EL device light emission, we can see that the scarlet light emission is very uniform at the whole emission area.

It should be pointed out that, from the EL spectra in Figure 3, it can be seen that the FWHM of the spectrum is only 50 nm, which suggests that the luminescent color of BAM is more monochromatic and is better suited for actual use in display technology without the need of filters. The reason for the narrower FWHM of BAM dye is not very clear now, for there are many factors to affect this phenomenon. Herein, we would like to offer a tentative explanation from both the electronic distribution viewpoint and the molecular geometric analysis of the BAM and DCMs molecules.

Compared with molecular structure of the broad bandwidth red dye DCMs (Figure 1), we can see that the molecular structure of DCMs is much different from that of the BAM, which means that BAM is a much symmetric molecule with the same electron donor groups of dimethylamine at two sides of the electron acceptor group of diaminomaleonitrile, respectively. Hence, in BAM molecule, there are two same charge transfer routes, which is from electron donor dimethylamine to diaminomaleonitrile; and in the DCMs molecules, e.g., DCM1, there are

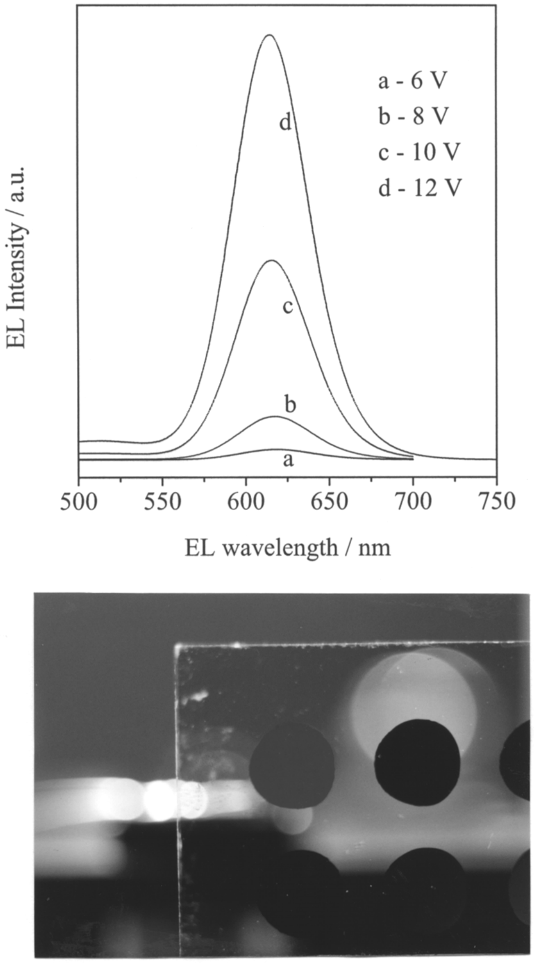


Figure 3. (Upper) The EL spectra of the double layer EL device under various bias voltages at room temperature. (Lower) Photograph of the EL emission.

two charge transfer routs, one comes from methyl group at C-6 position to dicyanomethylene group, the other is from electron donor dimethylamine to dicyanomethylene through a long conjugating system. So DCMs could be considered as two electron donors and two conjugated systems. Therefore, BAM might lead to less intramolecular or intermolecular exciton-photon coupling, which may have relation with a least change in transition dipole moment corresponding to red emission when excited. We postulate that the red light emitting materials, which have the same symmetric donor-acceptor structure, would also have narrow bandwidth.

On the other hand, molecular mechanics and orbital calculation by MOPAC program have revealed that the BAM molecule has linear structure, and it is very rigid, the BAM units could not be twisted around the molecular axis as shown in

Figure 4. From the analysis of the molecular structure of DCMs, which has either linear or planar structure, the functional group could twist around the molecular plane. It is well known that fluorescence is the emission of radiation from the lowest vibrational level of the excited singlet state S_1 to any of the vibrational levels of the ground electronic state S_0 in a molecule or ion. Therefore, there are less ground state vibrational levels S_0 in BAM molecules than those in DCMs molecules due to the rigid linear BAM molecular structure, which may somewhat contribute to the narrower bandwidth of BAM than that of DCMs.

Characteristics of the EL Device

The current-voltage (I-V) and luminance-voltage (EL-V) characteristics of the double-layer EL device are shown in Figure 5. It can be seen that luminance increases with injection current as well as drive voltage. The turn-on voltage was found to be approximately 6 V. Scarlet light with a maximum luminance of 6230 cd/m^2 was observed at 17 V, which is currently one of the brightest red light EL devices to the best of our knowledge. The luminance efficiency at a forward light output of 300 cd/m^2 is 1.1 lm/W. The inset of Figure 5 shows the chromaticity coordinates of the BAM doped EL device, which is x = 0.68, y = 0.32. The distinctive feature of this EL device is that no change in chromaticity coordinates was observed.

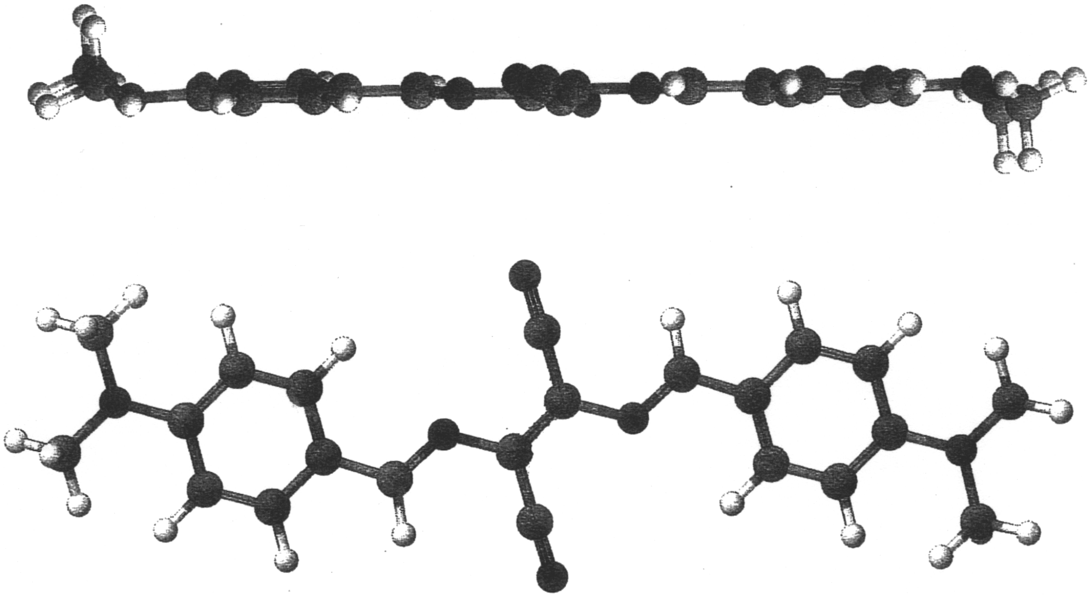


Figure 4. Molecular structure of BAM calculated by MOPAC: upper is the sheer review, and lower is the top view.

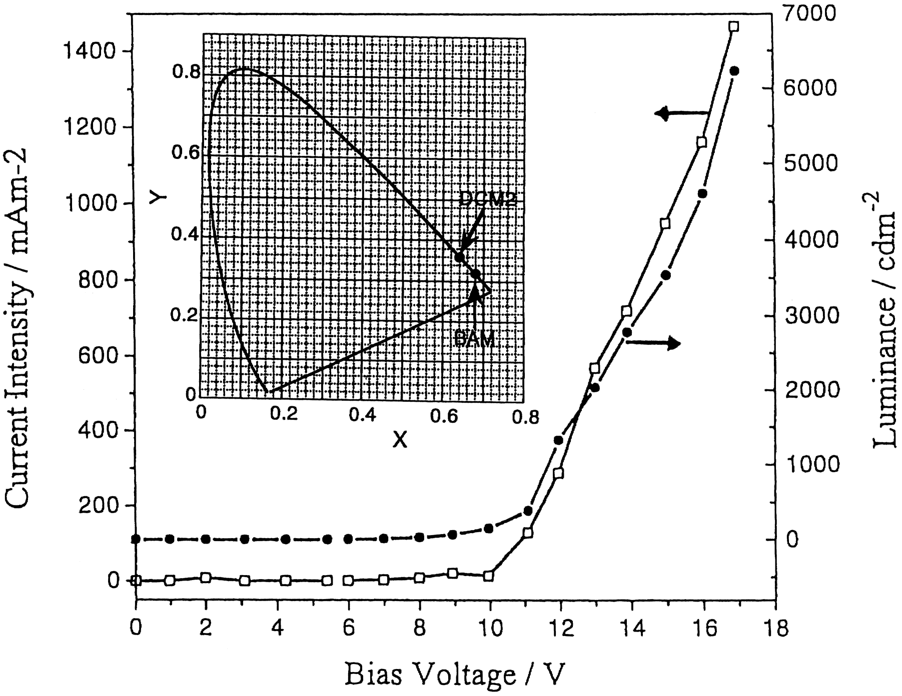


Figure 5. Current-bias voltage-luminance (I-V-EL) characteristics of double layer EL device. Inset: CIE chromaticity diagram showing chromaticity coordinates of BAM doped EL device, as well as the coordinates of the DCM2 doped device [13].

It is well known that device stability is a critical factor for the novel emitting materials, so both the performance of the BAM doped (1 mol%) device under storage and durability under continuous driving were investigated. As for the luminance change of the BAM doped device under long-term storage, luminance at the drive voltage of 10 V was measured regularly at one-day time interval. The device was detached from the darkroom and stored in a vacuum desiccator after every luminance measurement. It was found that during the first seven days, the luminance decreased gradually. The luminance on the seventh day reduced to 70% of the initial luminance. However, the luminance was almost remained constant during the following days (three weeks). As for the measurement of the durability of the BAM device under continuous driving at 10 V in the chamber evacuated by an oil rotary pump, the initial luminance dropped to its half value in 80 minutes. The intensity of the scarlet light continued to decrease to the low level over several hours and then remained at nearly steady level. The light was still visible in the darkroom after ten hours. The degradation mechanism of the BAM doped EL device is not clear now, but we assume that the degradation of the cathode should play a major role in the low vacuum circumstance.

CONCLUSION

The results reported in this study show that a novel red bisanil dye, N,N'-bis[4-(N, N-dimethylamino)-benzylidene] diaminomaleonitrile could be used as a red dopant to obtain a narrow bandwidth bright saturated scarlet light emission organic EL device. The luminance efficiency is about 1.1 lm/W and with the maximum luminance of 6230 cd/m^2. This is one of the best bilayer saturated red emission devices with narrow FWHM using very simple doping system. Further work including optimizing the device structure to increase luminance efficiency is under way now.

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