Single-layer white light-emitting organic electroluminescent devices based on dye-dispersed poly(*N*-vinylcarbazole)

J. Kido, H. Shionoya, and K. Nagai
Department of Materials Science and Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

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Bright single-layer white light-emitting organic electroluminescent devices were developed by using dye-dispersed poly(*N*-vinylcarbazole) (PVK). The active layer consists only of one polymer layer that is simply sandwiched between two electrodes, indium-tin oxide, and Mg:Ag. In order to achieve bipolarity in the single polymer emitter layer, PVK was molecularly dispersed with electron-transporting additives such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole. In addition, several fluorescent dyes, having different emission colors, were dispersed as emitting centers. By adjusting the concentration of the fluorescent dyes, white light with a maximum luminescence of 4100 cd/m^2 was obtained, which is the brightest white light ever observed for organic electroluminescent devices. © *1995 American Institute of Physics.*

Over the past few years, organic electroluminescent (EL) devices (or light-emitting diodes) have attracted much attention because of their high luminance, low drive voltage, and a variety of emission color. In these devices, electric energy is transformed into light through the excitation of the organic molecules.The excitation processes involve the injection of holes and electrons from the electrodes to the organic layer, and the recombination of these carriers generate excited molecules (excitons). Either low molecular weight materials[1] or high molecular polymeric materials[2] can be used as long as the material possesses appropriate carrier transport properties.

Recently, we have been interested in white light-emitting devices[3–5] because such devices have diverse applications such as illumination light source and backlight for a laptop computer. A full color display using a white light-emitting device and micropatterned color filters has also been proposed.[5] So far, we have developed two kinds of such devices: One is a multilayer device composed of a hole-transporting white light-emitter layer and electron transport layers.[3] The emitter layer is poly(*N*-vinylcarbazole) (PVK) which is molecularly dispersed with several fluorescent dyes to generate white light. The other type is also a multilayer-type device that consists of three emitter layers, each emitting in different color.[4]

In this study, our objective is to develop single-layer white light-emitting devices that consist only of one active organic layer. This type of device has a simpler structure than multilayer types; thus, the fabrication process is much simpler than that of the multilayer type. For example, we have developed single-layer-type devices with dye-dispersed polymers.[6,7] An electrically inert poly(methyl methacrylate) was molecularly dispersed with additives such as hole-transporting aromatic diamine derivative and electron-transporting aluminum chelate (Alq). From this device, green light, originating from Alq, with a luminance of 1000 cd/m^2 was obtained.[6] In this device, the color of the emitted light is tunable from green to red by further doping the polymer with an appropriate dopant.[7] However, it is impossible to obtain white light because the emission color of one of the carrier transport dopants Alq, is green; thus, blue light can not be obtained. Therefore, it is necessary to use carrier transport materials with emission color of blue or even the color with higher energy. To this end, we used PVK as a hole-transporting host polymer because it has electroluminescence in the purplish blue region,[8] and used electron-transporting additives that also possess high excited energy levels.

Because blue light is required as one of the three primary colors to obtain white light, we first attempted to obtain blue electroluminescence using two kinds of electron-transporting additives: In one device (type A), we used 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophen (BBOT), which also functions as a blue emitting center (fluorescence peak at ∼450 nm). BBOT has been known as an electron-transporting blue emitter, and used as an emitter layer in a multilayer EL device.[9] In the other device (type B), 2-(4-biphenylyl)-5-(4-tert-butylphenyl)1,3,4-oxadiazole (PBD) was used as an electron-transporting additive. Because PBD has a fluorescence peak at ∼390 nm, a blue emitting fluorescent dye, 1,1,4,4-tetraphenyl-1,3-butadiene (TPB), having a fluorescence peak at 430–450 nm was used as an emitting center. The cell configuration and the molecular structures of the materials used in this study are shown in Fig. 1

Device fabrication is a simple process. After coating an electrode surface with a polymer layer, cathode metal was vacuum deposited. In both devices, dichloroethane solutions containing PVK, having a molecular weight of 150 000 purchased from Kanto Chemical Ltd., and dopant dyes were prepared and dip coated onto an indium-tin oxide (ITO) coated glass substrate with a sheet resistance of 15 Ω per square. The thickness of the PVK layer was ∼1000 Å. Then, a 2000-Å-thick magnesium and silver (10:1) was codeposited on the organic layer surface as the top electrode at the same vacuum pressure. The deposition rates were maintained to be 11 Å/s.

Ionization potentials (I_p) of PVK film and the vacuum deposited films of organic dyes were determined from the wavelength dependence of photoemission of electrons using Riken Keiki AC-1, and the energy gap values E_g, were determined from the lower energy threshold of the electronic absorption spectra of the thin films of the materials. Then,

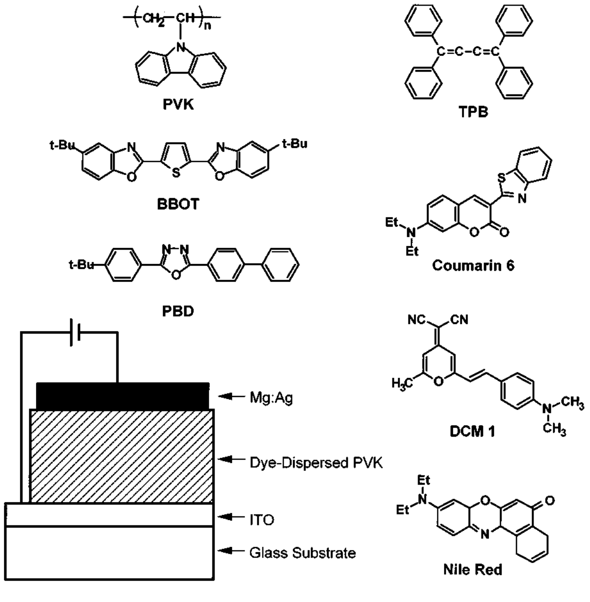

FIG. 1. Configuration of the EL device and molecular structures of materials used. The electron-injecting contact was made of an alloy of magnesium and silver (10:1) which was vacuum deposited from separate sources.

pseudoelectron affinities (E_a) were determined from I_p values and E_g values.[10]

In a type A device, hole-transporting PVK is doped with 30 wt % electron-transporting BBOT. From this device, bluish-green light was observed through the glass substrate when operated in a continuous dc mode with ITO at positive polarity. A luminance of 480 cd/m^{2}was obtained at 18 V. The EL spectrum consists of a broad peak at around 490 nm as shown in Fig. 2(A). Because a PVK film exhibits an emission peak at 410–420 nm and BBOT at 450 nm, it can be assumed that the peak seen at 490 nm may originate from the exciplex formed between the BBOT and carbazole group. Such exciplex formation has been observed between BBOT and aromatic diamine in a multilayer device.[9]

The color of the emitted light is in the blue-green region in the CIE coordinates in Fig. 3(A). To shift the color to the white region, the PVK layer is further doped with Nile Red. With 0.007 mol % Nile Red, the color moved to the white region as expected [Fig. 3(B)]. The spectrum in Fig. 2(B) consists of two peaks at 490 and 580 nm each from BBOT/carbazole exciplex and Nile Red, respectively. From this device, a maximum luminance of 1200 cd/m^2 is reached at 20 V, which is practically high.

In type B device, the electron transport additive used is PBD which has been used as an electron transport layer in multilayer EL devices[11] and also as an electron-transporting additive in single layer-type devices.[12,13] The use of PBD as an electron-transporting additive to PVK was first introduced by Mori and his co-workers.[12] They fabricated single-layer-type devices with PBD-doped PVK and obtained green light with Coumarin 6 and red light with DCM 1 as emitting centers, respectively. However, blue electroluminescence was not obtained. Very recently, Johnson *et al.* employed similar device structures using PVK and PBD,[13] but they have not obtained pure blue light but greenish blue light from the exciplex formed between the dopants.

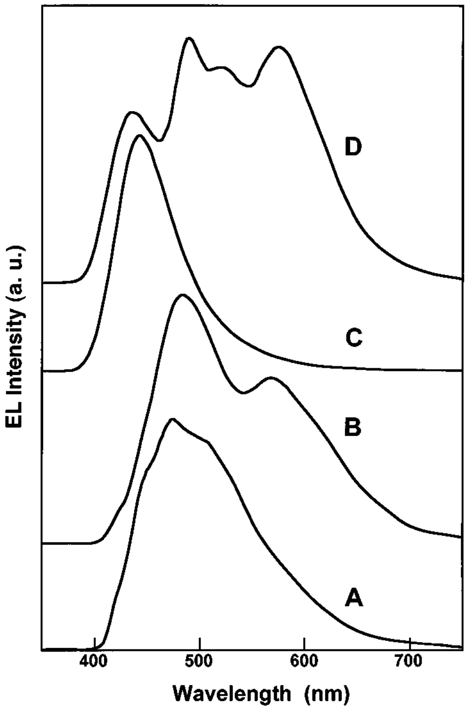

FIG. 2. Electroluminescence spectra of ITO/dye-dispersed PVK (1000 Å)/Mg:Ag devices. PVK is molecularly dispersed with (spectrum A) 30 wt % BBOT, (spectrum B) 30 wt % BBOT, and 0.007 mol % Nile Red, (spectrum C) 30 wt % PBD and 3 mol % TPB, (spectrum D) 3 mol % TPB, 30 wt % PBD, 0.04 mol % Coumarin 6, 0.02 mol % DCM 1, and 0.015 mol % Nile Red. These EL spectra were normalized and offset for clarity. These EL spectra were taken at a current density of 20 mA/cm^2 with an optical multichannel analyzer (Hamamatsu PMA 10).

The blue emitting dopant dye we chose is TPB which has been used by us as a blue emitting center in a PVK

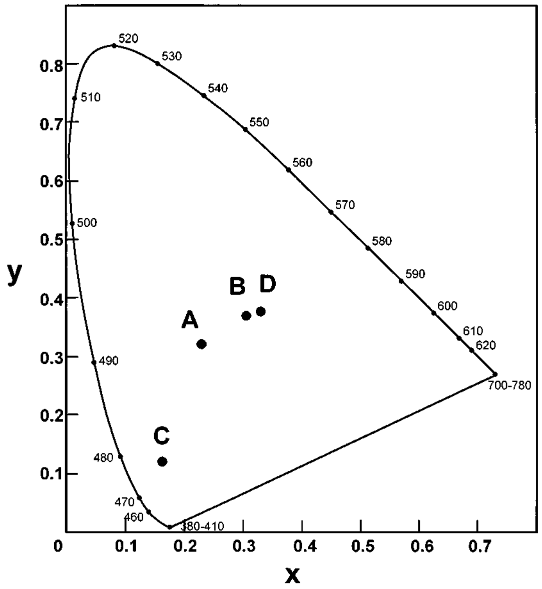

FIG. 3. CIE 1931 *x,y* chromaticity diagram. EL devices having PVK emitter layer dispersed with (A) 30 wt % BBOT, (B) 30 wt % BBOT, and 0.007 mol % Nile Red, (C) 30 wt % PBD and 3 mol % TPB, (D) 30 wt % PBD, 0.04 mol % Coumarin 6, 0.02 mol % DCM 1, and 0.015 mol % Nile Red.

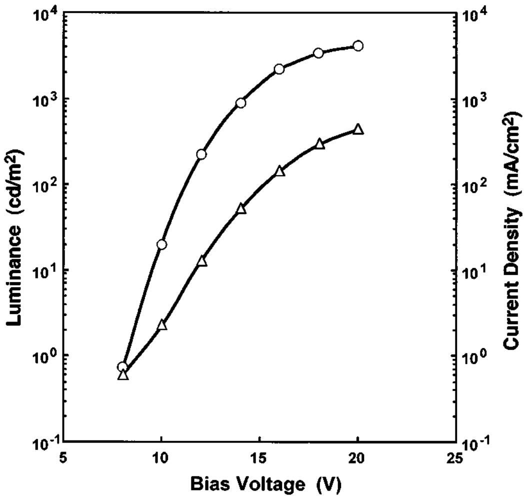

FIG. 4. Luminance–voltage (circles) and current–voltage (triangles) characteristics of a white-light emitting EL device (ITO)/dye-dispersed PVK (1000 Å) Mg:Ag, PVK is doped. The emitting area was 0.5×0.5 cm^2. Luminance was measured at room temperature with a Minolta LS-100 luminance meter.

emitter layer in multilayer devices.[3] With 3 mol % TPB doped to PVK that is also doped with 30 wt % PBD, the device emitted pure blue light having a peak at around 440 nm as shown in Figs. 2(C) and 3(C). Not only pure blue color, but a high luminance of 450 cd/m^2 was also achieved at 18 V, which is the highest value observed from single-layer blue light-emitting devices. The EL spectrum is identical to the photoluminescence spectrum of TPB, indicating that the emission originates from TPB. This implies that no exciplex is formed between the dopants. The color of the emitted light was then tuned to white by adding several fluorescent dyes with different fluorescent color such as Coumarin 6, DCM 1, and Nile Red as emitting centers. With appropriate concentrations of these dyes, white electroluminescence was obtained [Fig. 3(D)]. The EL spectrum differs widely from that of the PVK/BBOT device, which covers a wide range of the visible region from blue to red. As shown in Fig. 2(D), four peaks from the dopants were clearly seen: TPB at 440 nm, Coumarin 6 at 490 nm, DCM 1 at 520 nm, and Nile Red at 580 nm. The intensity of each peak can easily be changed by adjusting the concentration of the dopants; thus fine tuning of the emitted light is possible.

Luminance–voltage and current–voltage curves of the EL cell are shown in Fig. 4. Maximum luminance of 4100 cd/m^2 was reached at 20 V, which is, to the best of our knowledge, the highest value ever reported for white light-emitting organic EL devices. The large difference in luminance level between PVK/BBOT and PVK/PBD may be attributed to the low fluorescence quantum efficiency of the PVK/BBOT system due to the exciplex formed between BBOT and carbazole group.

Excitation mechanisms of each dopants are not fully understood at this moment. However, there are at least two possible mechanisms. One is energy transfer from the carrier transporting molecules (carbazole or PBD, or both) to the dopants via the Föster-type resonance energy transfer.[14] In this case, the excited energy is transferred from the host to the dopants that have appropriately lower excited energy levels relative to that of the host and the other is the so-called carrier trapping mechanism, in which dopants serve a carrier traps and provide recombination sites.[12,15] This type of excitation process is highly possible when the following conditions are met; that is, I_p of dopant is lower than that of host, and E_a of dopant is higher than that of host. In our systems, the orders of I_p and E_a values are I_p, TPB (6.0 eV)>PBD =BBOT (5.9 eV)>PVK (5.8 eV)>DCM 1 (5.6 eV) >Coumarin 6 (5.5 eV)>Nile Red (5.4 eV), and E_a, Nile Red=DCM 1 (3.5 eV)> Coumarin 6=TPB (3.2 eV) >BBOT (3.0 eV)>PBD (2.4 eV)>PVK (2.3 eV). Comparing I_p and E_a of the carrier transporters and the dopants, it can be assumed that TPB is mainly excited by the energy transfer because of its higher I_p than those of PVK and PBD, and Nile Red mainly by the carrier trapping because it serves as a deep hole trap as well as an electron trap. Both energy transfer and carrier trapping can be operative for the cases of Coumarin 6 and DCM 1. In addition to these mechanisms, energy transfer among dopants cannot be neglected. Thus, the excitation process is not quite simple in this system.

In conclusion, we succeeded to obtain bright white light that covers a wide range of the visible region by using a single layer structure. The most important factor to obtain bright white light seems to be obtaining bright blue light, which was realized by using appropriate dopant molecules to avoid exciplex formation. It is possible to lower the drive voltage by using hole-transporting polymers with lower ionization potentials, and electron-transporting additives with higher electron affinities. However, exciplex formation should be avoided to maintain the high quantum efficiency of fluorescent dyes.

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