Electroluminescent Poly(arylene ether) Containing Both Hole-Transporting and Electron-Transporting Units

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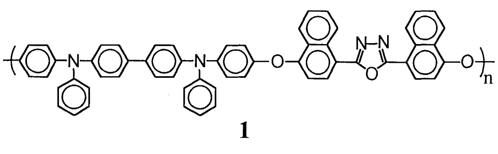
A poly(arylene ether) containing hole-transporting tetraphenylbenzidine units and electron-transporting 1,3,4-oxadiazole units was synthesized and examined as an emitter layer in organic electroluminescent device. The device structure of glass substrate / indium-tin oxide / polymer / Mg:Ag was employed. The EL device exhibited blue green light originating from the polymer emitter layer with a maximum luminance of 26 cd/m^2 at 12 volt.

Electroluminescence in organic materials has been investigated by a number of researchers for practical organic electroluminescent (EL) devices. Generation of light in such systems is the result of recombination of holes (radical cations) and electrons (radical anions) injected from the electrodes. Such recombinations in the emitter layer, then, produce the excitons (excited molecules). In order to achieve high carrier recombination efficiencies, a multilayer structure with a hole-transporting layer and an electron-transporting layer [1-3] or a single layer structure with bipolar carrier-transporting capability[4-10] is usually employed. For example, several single layer devices with a bipolar dye-dispersed polymer[5-9] as well as a bipolar polymer[10] have been reported.

In this study, our objective is to design and synthesize a bipolar polymer, being capable of transporting both electrons and holes, and to examine it as an emitter layer in single layer organic EL device. To realize high thermal stability, which is required for the active materials in EL device, poly(arylene ether) structure was employed. We have already demonstrated that poly(arylene ether)s containing tetraphenylbenzidine units have high thermal stability and serve as an excellent hole transport layer in multilayer EL devices.[11] To such a hole-transporting polymer, electron-transporting 1,3,4-oxadiazole units[9] were introduced into the polymer structure in order to achieve bipolar carrier-transporting capability, and used as an emitter layer in EL devices. The structure of polymer **1** synthesized in this study is shown below.



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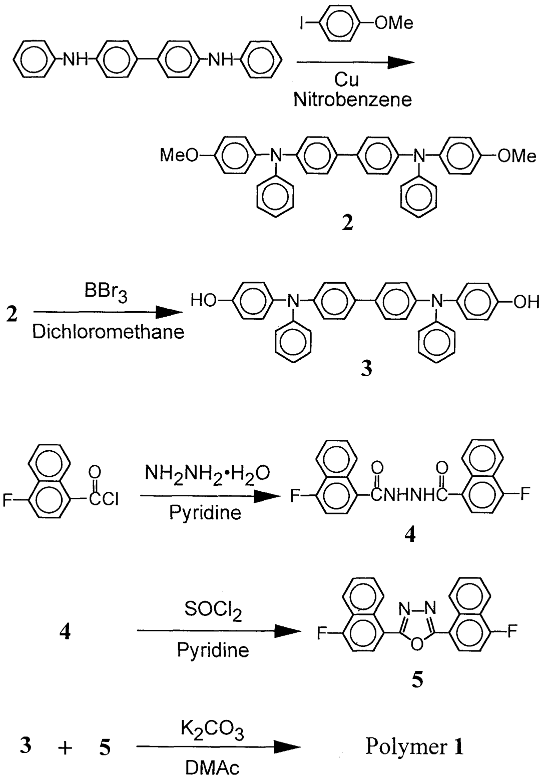

Schematic route of polymer **1** is shown in Scheme 1. Compound **2** was synthesized by the reaction of *N,N'*-diphenylbenzidine and 4-iodoanisole in nitrobenzene in the presence of activated copper at 220 °C, and was purified by column chromatography using silica gel (yield 58%). mp 158.0-159.2 °C. ^{1}H NMR (CDCl$_3$): δ6.82-7.40 (m., 26H, aromatic H), 3.80 (s., 6H, O-CH$_3$). IR (KBr): 1240 cm^{-1} (ν_{as} C-O-C), 1036 cm^{-1} (ν_s C-O-C). Found: C, 83.10; H, 5.92; N, 5.06%. Calcd for $C_{38}H_{32}N_2O_2$: C, 83.2; H, 5.88; N, 5.11%. Compound **2** was then reacted with boron tribromide in dichloromethane to afford compound **3**. The crude product was purified by recrystallization from cyclohexane/1,2-dichloroethane to give white needles in 43% yield; mp 232.8-234.2 °C. ^{1}H NMR (CDCl$_3$): δ6.75-7.50 (m., 26H, aromatic H). IR (KBr): 3534 cm^{-1} (ν O-H). Found: C, 82.42; H, 5.48; N, 5.26%. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.42; N, 5.38%. The synthesis of 2,5-bis(4-fluoro-1-naphthoyl)-1,3,4-oxadiazole **5** started from 4-fluoro-1-naphthoylchloride which was reacted with hydrazine monohydrate in pyridine at 120 °C for 6 h to give *N,N'*-4-fluoronaphthoylhydrazine, **4** (yield 66%). IR (KBr): 3180 cm^{-1} (ν N-H) The ring closure reaction of **4** in the presence of thionylchloride was conducted in pyridine at 80 °C for 3 h to give compound **5** (yield 96%). Compound **5** was purified by sublimation to give white powder in 74% yield; mp 278.9-280.0 °C. IR (KBr): 980 cm^{-1} (ν C-O-C) Found: C, 73.91; H, 3.57; N, 7.86%. Calcd for $C_{22}H_{12}N_2OF_2$: C, 73.74; H, 3.38; N, 7.82%.

Polymer **1** was synthesized by the reaction of compound **3** and compound **5** in *N,N*-dimethyacetamide in the presence of potassium carbonate at 140 °C for 14 h. ^{1}H NMR (CDCl$_3$): δ 9.40 (2H, aromatic H), 8.45 (2H, aromatic H), 8.20 (2H, aromatic H), 6.90-7.80 (m., 32H, aromatic H). Found: C, 83.11; H, 4.67; N, 6.83%. Calcd for $C_{58}H_{38}N_4O_3$: C, 83.04; H, 4.57; N, 6.68%. The polymer was purified three times by precipitation from chloroform solutions into methanol. The molecular weights of the polymer are $M_w = 9600$ and $M_n = 2900$

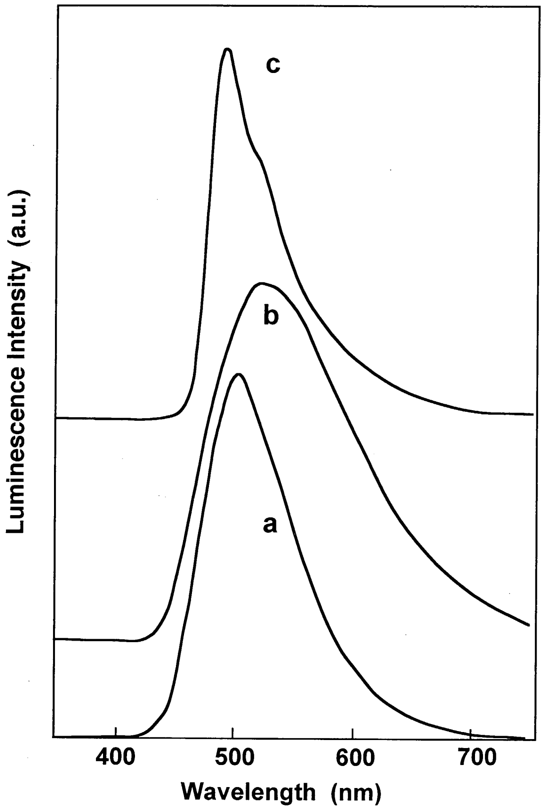

Figure 1. (a) PL spectrum of polymer **1** film, (b) EL spectrum of an ITO/polymer **1** (900 Å)/Mg:Ag device, (c) EL spectrum of an ITO/polymer **1** doped with 1 wt% of coumarin 6(900 Å)/Mg:Ag device. Spectra are offset for clarity.

as determined by gel permeation chromatography using polystyrene standards. The glass transition temperature of the polymer was determined to be 212 °C by differential scanning calorimetry.

Polymer **1** was used as an emitter layer in a single-layer-type device. The device structure is a glass substrate / indium-tin oxide (ITO) / Polymer **1** (900 Å) / Mg:Ag (10:1). The polymer layer was spin coated from chloroform solution onto an ITO-coated glass plate. The Mg:Ag top electrode was codeposited at 7.0×10^{-6} Torr. The emitting area was 0.5x0.5 cm^2. Luminance was measured with a Topcon BM-8 luminance meter at room temperature. Electroluminescence and photoluminescence (PL) spectra were taken on an optical multichannel analyzer (Hamamatsu Photonics K. K., PMA 10).

Blue green light was observed from the EL device when operated in a continuous dc mode with Mg:Ag negative. The EL spectrum in Figure 1 is similar to the PL spectrum of the spin coated film of the polymer. This indicates that electron-hole recombination occurs in the polymer layer, resulting in the excitation of the polymer. The emitting center is not clear at present, but exciplex formation between the diamine moiety and the oxadiazole moiety may be responsible for the blue green color of the emitted light.

The continuous dc current-voltage and luminance-voltage curves for the ITO / polymer **1** / Mg:Ag device are displayed in Figure 2. Luminance increased with increasing the injection current as well as the bias voltage. The maximum luminance of 26 cd/m^2 was obtained at 12 V. Doping the polymer layer with 1 wt% of coumarin 6 resulted in the emission from coumarin 6 (Figure 1c). In addition, the maximum luminance was improved to 100 cd/m^2.

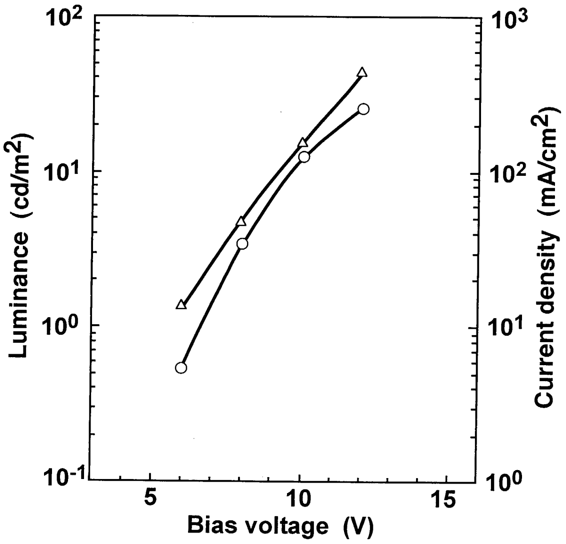

Figure 2. Luminance (circles) -current density (triangles) -voltage characteristics of an ITO/polymer **1**(900 Å)/Mg:Ag device.

In conclusion, we have synthesized a thermally stable carrier-transporting polymer that can be used as an emitter layer in organic EL devices. We are now modifying the polymer structure to improve recombination efficiency as well as fluorescence quantum efficiency.

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