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OLED Performance and the Use of a Hole Transport Molecule Dissolved in a High Tg Host Polymer

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Abstract

TPD has been dissolved in A435, a high Tg host polymer, in order to inhibit the crystallization of the hole transport molecule. Solid solutions of TPD have been obtained for a TPD content, x, ranging from 25 to 90 wt%. A435 + x TPD films coated onto ITO are stable during at least 72h at 150°C, for TPD contents of 50 wt% and below. OLEDs having the structure: ITO / A435 + x TPD/ Alq_3 /Mg have been prepared and measured. Maximum luminances of about 2000 cd/m^2 are obtained for $x \geq 50$ wt% TPD. The maximum quantum yield of these devices is 1.4%.

Introduction

TPD (N, N' - diphenyl- N,N'- di(m-tolyl) p-benzidine) has been used extensively as a molecular hole transport layer in the fabrication of organic light emitting diodes (OLEDs). However, TPD is known to have a rather low (~60°C) glass transition temperature (Tg). Hence, it has a tendency to crystallize under operating conditions affecting the quality and stability of the TPD-containing organic electroluminescent devices.

To circumvent this problem, hole transport molecules with higher Tg than that of TPD have been used.[1] Polymers with TPD-like functionalities as pendent groups or in the backbone have also been synthesized.[2] Another approach to improve resistance to crystallization is obtained by dissolving TPD in a high Tg host polymer, A435. This is the approach followed in this work. It will be shown that: (i) TPD forms solid solutions at all proportions in A435; (ii) it is possible to spin coat very smooth films of A435 + TPD when an appropriate combination of solvents is used to dissolve the composite; (iii) some of the A435 + TPD films remain amorphous depending upon the film support, its TPD content and the temperature; (iv) OLEDs made with A435 + TPD as hole transport layer and Alq_3 (8-hydroxyquinoline aluminum) as electron transport and emitting layer produce devices with useful brightness at moderate voltage.

Experimental

Synthesis of Amorphous Poly(Aryl Ether Ketone) (A435)

The synthesis of A435 previously described[3] was modified in order to minimize impurities. In a typical procedure, 6.4 x 10^{-3} mmole of bisphenol A (BPA), 12.8 x 10^{-3} mmole of potassium carbonate, 22 mL purified N,N'-dimethyl acetamide (DMAC) and 11 mL of toluene were added to a 100 mL three-necked flask equipped with a magnetic stir bar, a Dean-Stark trap, a cold water condensor, a thermometer and an argon inlet. The reaction mixture was heated to 130-140°C and refluxed for 2h to remove the water from the reaction system. In the process, the temperature gradually increased to 160°C. After the removal of the water, the temperature of the reaction system was decreased to 70°C, and 6.4 x 10^{-3} mmole of 1, 2 –bis (4-fluorobenzoyl) -3, 4, 5, 6- tetraphenyl benzene was then added into the flask with 10 mL toluene. 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbezene was synthesized according to ref. 3. The reaction mixture was heated again to refux at 135-140°C for 1 hour, and then to 150-160°C to remove most of the toluene and allowed the polymerization to proceed further for another 2 hours. During this time, the viscosity of the reaction mixture increased dramatically. After the polymerization was completed, the temperature of the reaction mixture was decreased to 70°C, and a solution of 0.1- 0.2 mL benzyl chloride in 5 mL toluene was injected into the flask. The temperature was increased to 150-160°C and kept for 1-1.5 hours so that the OH end groups of the polymer were capped completely.

The polymer purification process included 3 or 4 precipitation steps and 2 reverse precipitations. Finally, the polymer was dried in a drying pistol at 130°C under high vacuum overnight before being used. The yield of polymer A435 is 57%. The Tg of A435 is 252°C measured on a Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen. The molecular weight of the polymer was determined by GPC using polystyrenes as standards.[4-5] The Mn was 163,000, the Mw was 226,900 and the polydisperity was 1.4. The polymer was soluble in dichloromethane, chloroform, cyclohexanone, dioxane, anisole and tetrahydrofuran.

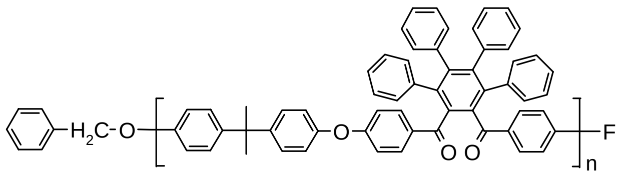

Figure 1. Host polymer A435.

OLED Preparation

ITO substrates (8Ω/sq.) were cleaned with methanol, then patterned by a rapid acid etching to obtain the anode of the devices. Patterned ITO substrates were cleaned in an acidic bichromate solution for 30 min, then rinsed with de-ionized water and hot acetone before being dried under N_2. The A435 + x TPD composite was then spin coated for 10 sec at 1000 rpm from a filtered solution (1.0 µm Whatman). Films of 70-80 nm thickness were obtained using that procedure. Alq_3 was vacuum sublimed at a residual pressure of about 1.5×10^{-5} mbar. After an initial degasing for 15 min at 200°C, Alq_3 was heated at about 230°C for 20 sec. Films of about 60 nm thickness were obtained using this procedure. The device was completed by vacuum deposition at about 1.5×10^{-6} mbar (in another system than Alq_3) of a Mg cathode of 0.8-1.0 µm thickness.

For all devices, current density, luminance and irradiance were measured as a function of the applied potential and apparent quantum yields were calculated from these measurements.

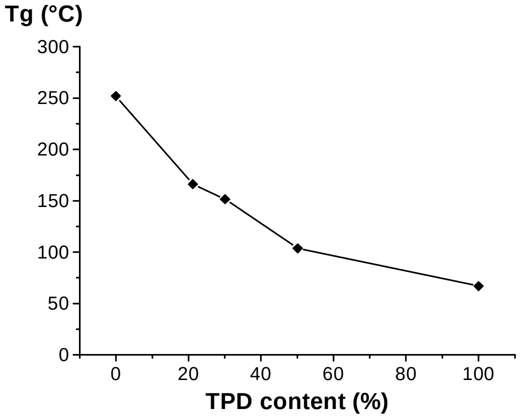

Figure 2. Change in the Tg of the A435 + TPD composite as a function of the TPD content.

Results

Solubility of TPD in Polymer A435 by DSC

The estimation of solubility of TPD in polymer A435 was done by carrying out measurements on the composite consisting of TPD and A435 with different amounts of TPD added. The solubility could be estimated by following the decrease in Tg with the increase of its concentration. At saturation, the Tg or Tm of TPD could additionally be observed. The DSC measurements of the composites were taken sequentially as follows: 3 steps of 30 to 280 °C to obtain and confirm the Tg of the composite, a 1 hour plateau at 160 °C to enable the TPD in the composite to crystallize, and another 30 to 280 °C step to measure the Tg.

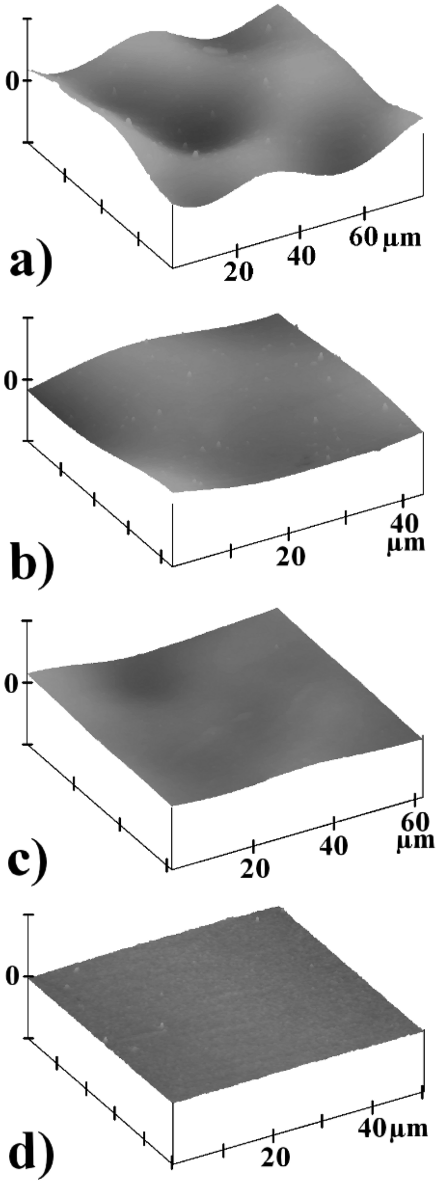

Figure 3. Morphology of A435 + x TPD composite films spin coated from a dichloromethane solution with x = 25 wt% (a), 50 wt% (b), and 75 wt% (c); or a dichloromethane + toluene solution with x = 25 wt% (d). The vertical range is 100 nm.

Neither the melting point or the Tg of TPD is observed in DSC measurements and the Tg of the composite decreases with the increase of the concentration of TPD in the composite. This is shown in Fig. 2. The change of Tg of the composite with the content of TPD is a rather smooth curve and thus suggests that TPD is completely miscible with A435.

Spin Coating of A435 + x TPD Films

Composite A435+ x TPD films with a TPD content of 25, 50, 75, and 90 wt% have been spin coated on glass and on ITO substrates from a dichloromethane solution. The thickness of these films decreases with increasing TPD content. Furthermore, Atomic Force Microscopy (AFM) reveals waviness at the surface of these films with larger amplitudes for lower TPD contents in A435. The morphology of these films is depicted in Fig. 3a to c for x = 25, 50, and 75 wt% of TPD, respectively. Devices made with these films had many shorts and low breakdown voltages.

Adding toluene in dichloromethane solved the film morphology problems. Fig. 3d displays the surface morphology of a film prepared by spin coating A435 + 25 wt% TPD from a 2 :1 (in volume) dichloromethane : toluene solution. A very smooth surface is indeed obtained on ITO and also on glass. Roughness measurements were made on all composite films on glass, with a TPD content going from 25 to 90 wt%. They indicated that the mean roughness value for all these films was about 1 nm. Good electrical behavior is therefore expected for devices using these films.

Annealing of A435 + x TPD Films

Annealing experiments were performed on A435 + x TPD films spin coated on glass and ITO from a dichloromethane + toluene solution. The TPD content was again varied between 25 to 90 wt%. All films were heated in a vacuum oven at two temperatures : 100 or 150 °C, for either 40 min, or 1, 2, 12, 24, 48, or 72h. For the sake of comparison, vacuum sublimed TPD films on glass slides and ITO were also heated at 100 and 150°C. The change in the morphology of these films with annealing conditions depends a lot on the nature of the film support. At 100 and 150°C, the pure TPD layer on glass melts before it has a chance to crystallize. On the other hand, on ITO, pure TPD does not melt at 100°C, so the crystallization process is observable during the first hour of annealing. The morphology of that film is depicted in Fig. 4a. For composite A435 + x TPD films, those with the higher TPD content are the first ones to show signs of crystallization. For instance, the first signs of crystallization appear after 48h at 100°C for A435 + 90 wt% TPD on glass., but the same film on ITO remains amorphous. When the annealing temperature is increased to 150°C, signs of crystallization of A435 + 90 wt% TPD films begin after one hour, even on ITO (see Fig. 4b). However, A435 + 50 wt% TPD on ITO and A 435 + 25 wt% TPD on ITO do not show any sign of crystallization even after 72h at 150°C (Fig. 4c). At that temperature, and according to Fig. 2, both compositions are above their Tg in bulk, but as thin films on ITO they remain amorphous.

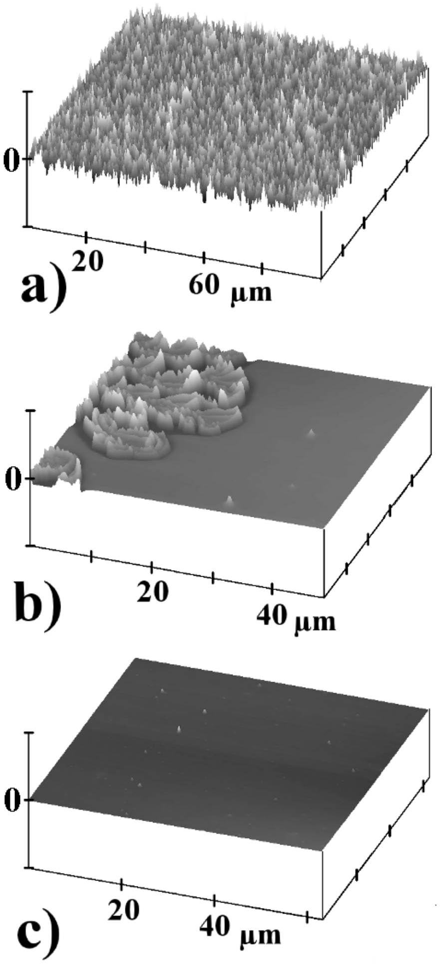

Figure 4. Morphology of thin films on ITO after annealing : (a) pure TPD after 1h at 100°C; (b) A435 + 90 wt% TPD after 1h at 150°C; (c) A435 + 25 or 50 wt% TPD after 72h at 150°C. The vertical range is 100 nm.

OLED Devices

All devices having the structure : ITO / A435 + x TPD / Alq_3 / Mg display a diode-like current-voltage (I-V) curve. The luminance-voltage curve follows the I-V curve's behavior.

Fig. 5 depicts the evolution of the threshold field with the TPD content. As expected, it shows a linear dependence with lower threshold fields for higher TPD contents. These fields correspond to about 13 and 8 Volts for 25 and 90 wt% TPD, respectively.

The evolution of the maximum luminance of the devices is presented in Fig. 6. It shows that a step in maximum luminance occurs between x = 25 and 50 wt% TPD. Furthermore, there is little difference between the luminance of the devices once 50 wt% TPD is reached. A maximum efficiency of 1.4% is obtained for TPD contents ≥ 50 wt% while 0.9% is achieved at their maximum luminance.

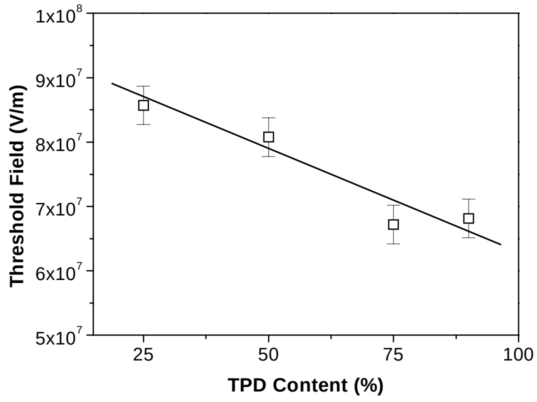

Figure 5. Change in the device threshold field with the TPD content.

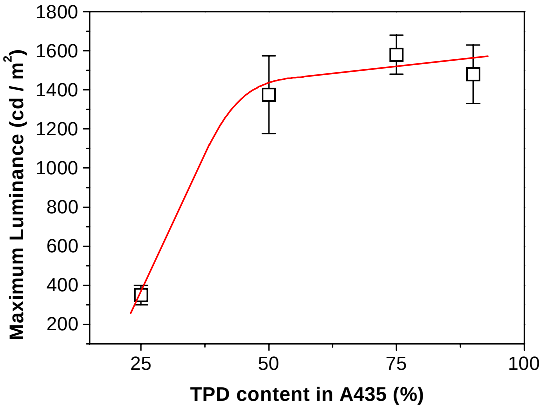

Figure 6. Change in the luminance of the device with the TPD content.

All devices display the typical electroluminescence spectrum of Alq_3 with a maximum at 510 nm in the green.

Conclusion

On the one hand, amorphous hole transport layers containing up to 50 wt% TPD in A435, a high Tg host polymer, have been demonstrated to be rather stable upon annealing even at temperatures as high as 150°C. On the other hand, bright devices are obtained for TPD contents as low as 50 wt% and higher TPD contents do not seem to have a large influence on the luminance of the devices. Therefore it seems that devices made with A435 + 50 wt% TPD would be the best choice for high stability to avoid recrystallization while still providing a high luminance. The stability of such devices is now under investigation.

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