Double Spin-Coated Organic Electroluminescent Devices

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Abstract

New electroluminescent (EL) molecules, dissolved in a high T_g poly(aryl-ketone) (A435), have been used in double spin-coated electroluminescent devices. The first EL molecule is a soluble AlQ_3 derivative and the second one is a hexaphenyl-substituted isobenzofuran. The maximum solubility of both EL molecules in A435 is about 70 wt%. The typical structure of the devices is: [ITO/HTL/ETL/Mg], where HTL is a new high T_g hole transport aryl amine polymer and ETL is one of the new EL molecules in solid solution in A435. HTL is spin-coated from chloroform while the second layer is spin-coated from toluene. HTL is completely insoluble in toluene. For the devices prepared with the AlQ_3 soluble derivative or for the devices prepared with the hexaphenyl-substituted isobenzofuran, the luminance has been found to increase with the EL molecule content (up to 50 ± 5 wt%) in A435. Maximum luminance values higher than 2000 cd/m^2 have been measured for the soluble AlQ_3 (peak emission at 545 nm) while they reach 1000 cd/m^2 for the isobenzofuran derivative (peak emission at 505 nm). The luminance decreases drastically when the EL molecule content in A435 increases above 50 wt%. The current density in both double spin-coated OLEDs is quite large affecting therefore their quantum efficiency. Solutions to improve the quantum efficiency are described.

Introduction

Active materials used in organic light emitting diodes (OLEDs) may be roughly divided into two groups: (i) small molecules which can be vacuum sublimed and (ii) polymers which are solution-processed. In the small molecule group, the functions of hole and electron transport are generally performed by different molecules.[1] The archetype of hole transport (HT) molecules is arylamines while that of electron transport (ET) materials is AlQ_3 (8-hydroxyquinoline aluminum).[2] Both hole and electron transport molecules are vacuum sublimed consecutively onto a transparent anode (usually indium-tin oxide : ITO) The device is completed by the evaporation of a low work function cathode (like Mg or Mg-Ag).

The use of two different molecular layers to transport holes and electrons reduces non-radiative carrier annihilation at the injecting contacts and allows for carrier localization and recombination at the potential barriers near the HT/ET interface. In the special case of AlQ_3, the same molecule transports electrons and is also the source of the luminescence. Due to the specificity in the type of charges transported by HT or ET molecules and the difference in their energy levels, direct neutralization of holes at the cathode and electrons at the anode is avoided. This, with exciton confinement at the molecular interface, greatly improves the quantum efficiency and the luminance of molecular devices (luminance values up to 140,000 cd/m^2 have been claimed.[3]

For polymer light emitting devices, the same material is able to transport holes and electrons as well as serve as the source of the luminescence.[4,5] The archetype of polymer light emitting material is PPV (poly(p-phenylene vinylene)). It has however been demonstrated that - using a first layer of PPV and a second layer of a polymer with a high electron affinity - the efficiency of these devices can be greatly improved.[6]

Our approach in designing materials for light emitting devices is situated between the two presented approaches. Indeed, active molecules were used as hole or electron transport materials but they were integrated as functionalities in the structure of high T_g polymers[7,8] or were dissolved in high T_g host polymers.[9] The problem when two polymer layers have to be superimposed in a device is that the already solvent-processed first layer should not be soluble in the solvent used to process the second layer. In the case of PPV mentioned above, it is the precursor of PPV which is spin-coated. This layer is then heat converted to PPV which becomes insoluble in chloroform, the solvent of the high electron affinity polymer used in the second layer. In the present work, we are playing on the relative agressivity of two solvents, using the less agressive solvent to spin-coat the second polymer. Two examples of double spin-coated devices will be given. The hole transport polymer NPB-QP (see **results and discussion** for its structure) is common to both types of devices. This polymer contains a tertiary arylamine copolymerized with a quaterphenyl-based moiety which is used to modify the

solubility of the resulting copolymer. The electron transport and electroluminescent layer is either made of A435, a transparent host polymer, and a soluble AlQ_3 derivative or a soluble isobenzofuran derivative.

Experimental Section

Materials. Benzene, benzylchloride, bromine, cyclohexa-1,4-diene, 5,7-dibromo-8-hydroxyquinoline, 8-hydroxy-quinoline, phenylboronic acid, potassium carbonate, potassium iodide, palladium on activated carbon (10wt%), sodium bicarbonate, sodium carbonate, sodium hydroxide, tetrahydrofuran (THF), tetrakis(tetraphenylphosphine) palladium ($Pd(PPh_3)_4$), and triethylaluminum (1.9 M solution in toluene) were purchased from Aldrich Chemical Co. and used as received. Anhydrous THF was obtained by a distillation in the presence of sodium.

Synthesis of Intermediates to ALDPQ
5,7-dibromo-8-benzyloxyquinoline (*2*)

A mixture of 5,7-dibromo-8-hydroxyquinoline (5.0 g, 16.5 mmol), potassium carbonate (2.28 g, 16.5 mmol), benzyl chloride (2.3 g, 18.2 mmol), and potassium iodide (0.27 g) in acetone (100 mL) was refluxed under N_2 for 10 hr. The mixture was poured into water, filtrated and washed with water. The residue was recrystallized from ethanol and dried in vacuo (yield : 91 %). ^{1}H-NMR (TMS/CDCl$_3$, ppm): δ = 5.48 (2H, s), 7.30-7.40 (4H,m), 7.54 (1H, dd), 7.62 (1H, dd), 7.98 (1H, s), 8.47 (1H, dd), 8.98 (1H, dd). ^{13}C-NMR (TMS/CDCl$_3$, ppm): δ = 76.8 (CH$_2$), 116.5, 117.0, 122.7, 128.3, 128.4, 128.6, 128.9, 133.8, 136.2, 137.2, 144.1, 150.9, 152.5. MALDI: 393 (calc. 393).

5,7-diphenyl-8-benzyloxyquinoline (*3*)

A mixture of 5,7-dibromo-8-benzyloxyquinoline (2.0 g, 5.1 mmol), phenylboronic acid (1.37 g, 11.2 mmol), benzene (20 mL), ethanol (10 mL), water (15 mL) and sodium carbonate (2.15 g, 20.3 mmol) was degassed under N_2 for 30 min. To the mixture was added $Pd(PPh_3)_4$ (353 mg, 0.31 mmol), and the reaction was refluxed under N_2 for 24 h. The crude product was extracted with benzene, recrystallized from ethanol, and dried in vacuo (yield: 89 %). ^{1}H-NMR (TMS/CDCl$_3$, ppm) : δ = 5.19 (2H, s), 7.21 (5H, s), 7.36-7.47 (9H, m), 7.49 (4H, d), 7.55 (1H, s), 7.67 (2H, dd), 8.26 (1H, dd), 9.05 (1H, dd). ^{13}C-NMR (TMS/CDCl$_3$, ppm) : δ = 77.3 (CH$_2$), 115.9, 121.4, 127.7, 127.8, 127.8, 128.3, 128.4, 128.7, 129.8, 130.0, 130.3, 130.4, 134.2, 134.8, 136.2, 137.7, 138.4, 139.4, 143.8, 149.7, 151.2. MALDI: 387 (calc. 387).

5,7-diphenyl-8-hydroxyquinoline (*4*)

A mixture of 5,7-diphenyl-8-benzyloxyquinoline (1.4 g, 3.6 mmol), Pd/C (10 wt%, 1.1 g) and cyclohexa-1,4-diene (2.6 g) in absolute ethanol (35 mL) was refluxed under N_2 for 10 h. The mixture was filtrated, and ethanol was evaporated. The product was recrystallized from ethanol-water and dried in vacuo (yield: 90 %). ^{1}H-NMR (TMS/CDCl$_3$, ppm): δ = 7.34-7.51 (10H, m), 7.62 (1H, s),

7.84 (1H, dd), 8.28 (1H, dd), 8.80 (1H, dd), 8.88 (1H, s, OH). ^{13}C-NMR (TMS/CDCl$_3$, ppm): δ = 121.9, 122.4, 126.1, 127.5, 127.6, 128.7, 128.8, 129.6, 130.2, 130.4, 130.9, 134.9, 137.8, 138.9, 139.5, 148.1, 148.4. . MALDI: 297 (calc. 297). Mp: 138 °C.

Tris(5,7-diphenyl-8-quinolinolate-N1,O8)aluminum (ALDPQ, 5)

To a solution of 5,7-diphenyl-8-hydroxyquinoline (800 mg, 2.69 mmol) in anhydrous THF (40 mL) was slowly added triethylalminum (102 mg, 0.894 mmol, commercially available 1.9 M toluene solution was used). The mixture was stirred for 48 h at room temperature under N_2, and THF was evaporated. The product was recrystallized from ethanol-hexane and dried in vacuo (yield: 93 %). ^{1}H-NMR (TMS/CDCl$_3$, ppm) : δ = 7.17-7.45 (m), 7.77, 7.88, 7.97, 8.2, 8.30-8.36(m), 8.81. ^{13}C-NMR (TMS/CDCl$_3$, ppm): δ = 120.9, 121.7, 122.8, 123.9, 124.7, 125.3 , 126.5, 127.1, 128.3, 128.8, 129.1, 130.3, 132.1, 132.8, 137.8, 138.5, 139.1, 139.8, 140.7, 142.9, 145.0, 145.8, 156.3, 157.0. MALDI: 916 (calc. 916). Tg: 213 °C. Td$_{5\%}$: 512 °C

OLED's Preparation and Tests

ITO substrates (15 $\Omega/\square$; Applied Films Corporation) were cleaned with methanol, then patterned by a rapid acid etching with Zn and HCl to obtain the anode of the devices. Patterned ITO substrates were cleaned in an acidic bichromate solution for 30 min, then rinsed with de-ionised water and placed in a ultrasonic bath of ethanol. The cleaned substrates were then rinsed with methanol before being dried under N_2. Devices were fabricated at ambient conditions by spin coating the filtered hole transport polymer (NPB-QP) solution in chloroform (3mg/ml) on the ITO substrates at 600-700 rpm. The thickness of the NPB-QP layer was typically ~ 35 nm. The second organic layer consisted of either the electroluminescent ALDPQ or B1533 molecules dissolved in A435, spin coated at 700 rpm from their toluene solution (13 mg/ml). The thickness of the second organic layer was typically 55 ± 10 nm. Because NPB-QP is not soluble in toluene, the first layer is not affected by the coating. Then, a layer of magnesium (100-150 nm thick) was vacuum deposited at 2.10^{-6} Torr through a mask to obtain the cathodes. Five OLEDs were fabricated at the same time on the same ITO substrate. The dimensions of each OLED were 2 x 13 mm^2.

Current-Voltage and Luminance-Voltage curves were recorded at the same time in Ar atmosphere. The voltage source was a 175 EG&G Universal Programmer. Luminance was measured with a Tektronix Lumacolor II photometer, Model J18. Electroluminescence spectra were recorded using a monochromator (ISA Instruments), a photomultiplier and a photometer (Pacific Precision Instruments, Model 126).
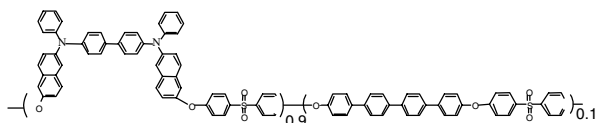
Results and Discussion

Polymeric Hosts and Electroluminescent Molecules

The synthesis of amorphous poly(aryl ether ketone) (A435) has been described previously.[9] The aryl amine polymer (NPB-QP) synthesis will be described in a future publication. The T_g of A435 is 252°C and that of NPB-QP is 256°C.
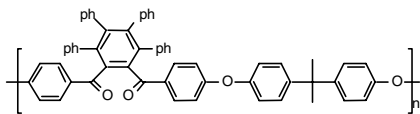
Host polymer A435

Hole Transport Polymer NPBQP

We have synthesized AlDPQ, a derivative of Alq_3 derived from 5,7-diphenyl-8-hydroxyquinoline, 4. The general methodology used by Nakano for the synthesis of 5-phenyl-8-hydroxyquinoline was used (10). The benzyl derivative of 5,7-dibromo-8-hydroxyquinoline, 2, was first synthesized which then underwent a Suzuki coupling reaction with phenylboronic acid to give 3. Debenzylation gave 4 and then 4 was then reacted with triethylaluminum to give the complex 5. AlDPQ is soluble in A435 at least up to 70 wt%, as measured by differential scanning calorimetry.

The preparation of 1,3,4,5,6,7-hexaphenyl-isobenzo-furan, **6**, has been described previously.[11] The method used by Zweig for the synthesis of a related compound was used.[12] The isobenzofuran **6** is soluble in A435 at least up to 70 wt% as measured by differential scanning calorimetry.
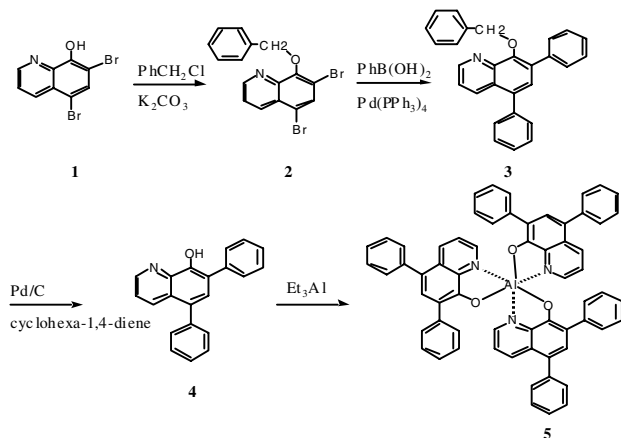
Synthesis route for ALDPQ
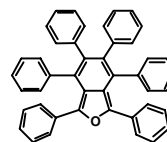
1,3,4,5,6,7-hexaphenyl isobenzofuran (B1553)

Characterization of AlDPQ-Based Devices

Double spin coated devices of the type : [ITO/ NPB-QP/ A435 + x AlDPQ/ Mg], where x is the wt% of AlDPQ in A435, are emitting green light. The EL spectrum of a device with x = 50 wt% of AlDPQ is shown in Fig. 1.
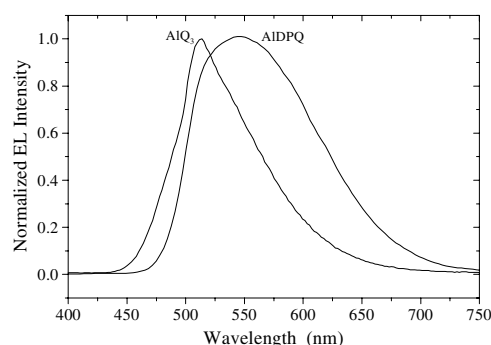

Figure 1. Electroluminescence spectrum of an OLED containing 50 wt% AlDPQ in A435. The EL spectrum of vacuum sublimed AlQ_3 is given for comparison.

The EL band is broad with a maximum at ~ 545 nm. The presence of additional phenyl rings on the hydroxy-quinoline complexing aluminum red shifts the spectrum by about 30 nm compared to the EL spectrum of vacuum sublimed AlQ_3 which is given in Fig. 1 for comparison.

OLEDs with different AlDPQ contents (between 20 and 73 wt% in A435) have been studied. All devices display a typical diode-like Current-Voltage curve which is presented in Fig. 2 for x = 50 wt% AlDPQ. Figure 2 also shows the Luminance-Voltage curve of the same device. The device has a low turn on voltage of 6 V. Its luminance reaches 2220 cd/m^2 at a bias voltage of 23V and a current density of 920 mA/cm^2, corresponding to an external quantum efficiency of 0.2%.

Fig. 3A presents typical changes in the Luminance at a constant current density of 250 mA/cm^2 for devices using A435 + x AlDPQ with x varying from 20 to 73 wt%. This graph shows that the luminance increases first with the AlDPQ content up to ~ 1100 cd/m^2 for x = 50 wt%, then decreases. The quantum yield at maximum luminance in Fig. 3A is 0.39 %. The increase in luminance is related to the increase in the density of individual electroluminescent centers.
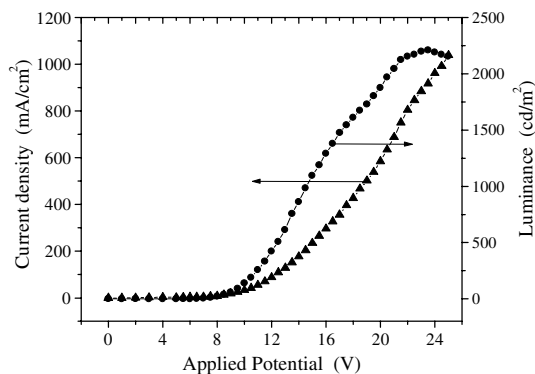
Figure 2. Current-Voltage and Luminance-Voltage characteristics of an OLED containing 50 wt% of AlDPQ in A435
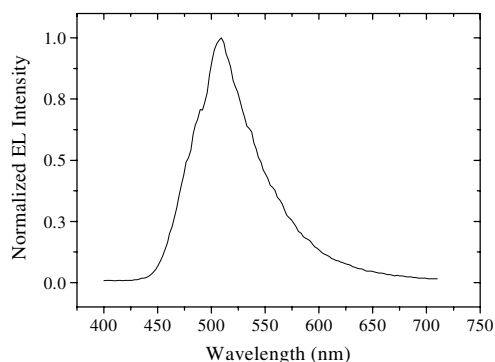

Figure. 4. Typical electroluminescent spectrum of an OLED containing 50 wt% B1553 in A435.
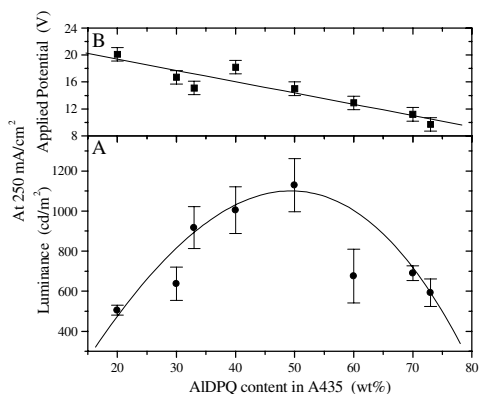

Figure 3. A:Change in the Luminance (at a current density of 250 mA/cm^2) with the AlDPQ content; B: Applied potential required to obtain 250 mA/cm^2.

Figure 5. Current-Voltage and Luminance-Voltage characteristics of an OLED containing 50 wt% of B1553 in A435

The problem is to explain why the luminance saturates then decreases when it is known by DSC that AlDPQ is soluble in A435 at least up to 70 wt%. However, these solubilities are measured at the T_g of the blend (219°C in the present case), and the solubility at room temperature may be somewhat lower. Therefore, it is proposed that the association of AlDPQ in a separate phase quenches the luminance of AlDPQ molecules dissolved in the solid solution. An alternative explanation based on a decrease in the device conductance does not hold. Indeed, it is shown in Fig. 3B that the applied potential necessary to obtain 250 mA/cm^2 decreases with increasing the AlDPQ content. This corresponds to a monotonous improvement of the conductance as the AlDPQ content increases and the luminance decreases.

Characterization of B1553-based devices

Double spin-coated devices of the type : [ITO/ NPB-QP/ A435 + x B1553/ Mg] also emit green light too. The EL spectrum of a device with x = 50 wt% B1553 is shown in Fig. 4.
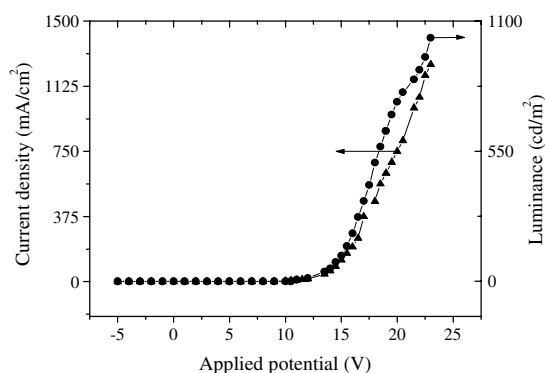
OLEDs with different B1553 contents have been studied. Fig. 5 displays the Current-Voltage curve of an OLED containing 50 wt% B1553. Its luminance reaches a maximum of 1020 cd/m^2 at 1.25 A/cm^2, corresponding to an efficiency of 0.06 %.

Fig. 6A presents typical changes in the Luminance at a constant current density of 250 mA/cm^2 for devices using A435 + x B1553. Fig. 6B presents the applied potential necessary to obtain 250 mA/cm^2 for each B1553 content. Both Fig. 6 and 3 are similar and the explanation given for AlDPQ in Fig. 3 also applies to B1553 in Fig. 6. It was also determined by DSC that B1553 was soluble at least up to 70 wt% in A435 at the Tg of the blend. The quantum yield at maximum luminance in Fig. 5A is 0.1 %.

Improving the Devices

Even if all devices are not completely optimized, the current densities observed for these double spin coated OLEDs are quite large. This results in low quantum efficiencies. Attempts have been made to improve the quantum efficiency of the devices based on AlDPQ. First,

PBD, an oxadiazole derivative was dissolved in A435 + AlDPQ in order to determine the effect of improving the electron transport properties of that layer. PBD is indeed known as an electron transport molecule.[13] Adding 25 wt% PBD in A435 + 50 wt% AlDPQ nearly doubled the luminance and the quantum efficiency of that device at 250 mA/cm^2. The Electroluminescent spectrum of the device was not affected. In a second attempt to improve the quantum efficiency of the device, a thin layer of Bathocuproine (BCP) was inserted by vacuum sublimation between the cathode and the emitting layer. Bathocuproine is known as an electron transport material and a good hole blocking material.[14,15] The quantum efficiency of a device containing the sequence : [ITO/ NPBQP/ A435 + 50 wt% AlDPQ/ BCP/ Mg] is improved by a factor of 3 at 250 mA/cm^2 using the BCP layer.
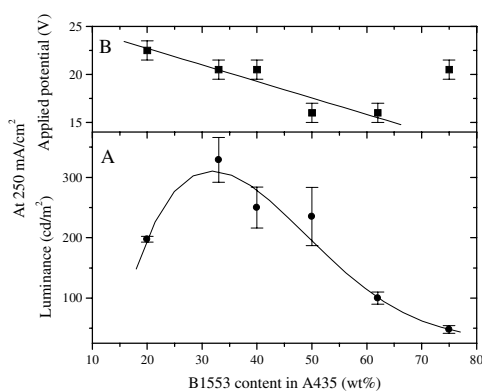

Figure 6. A: Change in Luminance (at a current density of 250 mA/cm^2) with the B1553 content; B: Applied potential required to obtain 250 mA/cm^2.

Conclusions

It is possible to obtain double spin-coated OLEDs with interesting brightnesses. In these devices, the first layer is a hole transport polymer (NPB-QP) spin coated from a solution in chloroform, while the second layer is an AlQ$_3$ derivative (or an isobenzofuran derivative) molecularly dispersed in A435, a host polymer, spin coated from a solution in toluene. The OLED luminance changes with the content of the AlQ$_3$ derivative or the isobenzofuran derivative in the ET layer, going through a maximum for contents of about 50 ± 5 wt%. In both cases studied, large currents have been observed which affect the quantum yield of the devices. It is, however, possible to increase the quantum yield of these devices by improving the transport properties in the ET layer and by inserting a hole blocking material between the ET layer and the cathode.

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Biography

Jean-Pol DODELET is a physical chemist with interest in optoelectronic properties of organic materials. He is Professor at INRS Energie et Materiaux, a research center of University of Quebec. He has been working on OLEDs for about two years in collaboration with Allan S. Hay from McGill University, Marie D'Iorio from the National Research Council of Canada, and the Company: Luxell Technologies. The work of the group is focused on the use of active molecules in solution in high Tg soluble host polymers or active molecules in the structure of the high Tg soluble polymers.