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Efficient Silole-Based Organic Light-Emitting Diodes Using High Conductivity Polymer Anodes

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High luminance organic light-emitting diodes (OLEDs) with a relatively low operating voltage are presented using a conducting polymer [without an indium−tin oxide (ITO) underlayer] as a hole-injecting electrode (anode) and silole derivatives as an emitter and/or an electron transporter. The conducting polymer films of poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) were either spin-cast from aqueous dispersions on glass substrates or supplied as precoated films on poly(ethylene terephphalate) substrates. The films obtained by spin casting on glass substrates show very low sheet resistance (150 Ω/sq). OLEDs fabricated using this conducting polymer as an anode without using an ITO underlayer and CsF/Al as a cathode exhibit very low operating voltages (6.5 V at 1000 cd/m^2). The silole derivative, 2,5-bis-(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene, used as an electron transporter, forms an Ohmic contact with the electron-injecting electrode (CsF/Al), leading to efficient electron injection. This contributes to better charge balance and improved device efficiency.

Introduction

Indium−tin oxide (ITO) is the most widely used electrode material in displays such as liquid crystal displays (LCDs) and organic light-emitting displays (OLEDs), since it is highly conductive and transparent in the visible region (400−800 nm).[1−3] However, ITO is very brittle and is not suitable for flexible devices, since it tends to deform upon bending and easily delaminates. A recent study shows that the surface sheet resistance of ITO on plastic substrates is very sensitive to bending.[4] A significant increase in the surface sheet resistance (∼2 orders of magnitude) is observed when the plastic substrate is either bent below an 8 mm bending diameter or undergoes a multiple bending process with larger bending radii. This effect is not desirable for flexible displays where the device performance such as brightness and operating voltage is greatly affected by a change in the anode surface resistance. On the other hand, a conducting polymer electrode on a plastic substrate (100 nm thickness) was found to maintain its original conductivity when exposed to the same mechanical stress.[4] No noticeable change in surface resistance and morphology was observed. Conducting polymers are ideal in this respect, especially for display applications, where the operating voltage is sensitive to the change in surface resistance. However, their present sheet resistance values are still too high for practical usage in displays and solid-state lighting applications.

Since the first report of metallic behavior from the doped polyacetylene reported by Shirakawa et al. in 1977,[5] various conducting polymers have been developed and there are a few conducting polymers commercially available in the market. Among them, poly(3,4-ethylenedioxythiophene)−polystyrenesulfonate (PEDOT:PSS), first introduced in the 1990s by Bayer AG Germany, has been most widely used in many electronic and optoelectronic applications such as an antistatic coating in photographic films, an electrode material for capacitors, and in printed circuit boards and microactuators.[6,7] PEDOT:PSS offers many advantages due to its ease of processability, good film-forming properties, high optical transparency in the visible region, and good mechanical strength. High atmospheric stability is another attractive property of PEDOT:PSS.[6] However, the electrical conductivity of this polymer (∼10 S/cm) is still low for OLED and LCD applications, where device performance is greatly affected by the surface sheet resistance of the electrode.

Much effort has been focused to further increase the conductivity of PEDOT:PSS.[8−15] In most cases, one to

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two orders of magnitude increase in conductivity was observed and was accompanied by a decrease in optical transmittance. The most surprising results were obtained from the PEDOT:PSS films doped with a small amount of polyalcohols or high boiling point solvents.[12−15] In contrast to conventional oxidative (protonic) doping, where the enhancement of the electrical conductivity (or decrease in surface sheet resistance) is always accompanied by a decrease in optical transmittance due to the absorption of radical cations (polarons) in the visible region,[16] no change in optical transparency was measured for the PEDOT:PSS films doped with polyalcohols or other high boiling point liquids. For example, a dramatic decrease in surface sheet resistance from 7.1 to 1.8 kΩ/sq was observed upon doping with glycerol with no change in optical transparency. Recently, we have demonstrated that OLEDs using this highly conductive polymer anode (without an ITO underlayer) exhibits an enhanced performance compared to that using a standard PEDOT:PSS film, i.e., without any added polyalcohol as an anode.[17,18] Devices based on a bilayer structure of *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis-(phenyl)benzidine (α-NPB) as a hole-transporting layer and tris(8-hydroxyquinolinolato)aluminum(III) (Alq$_3$) as the electron transporter/light-emitter and using this chemically modified conducting polymer as an anode with Mg:Ag cathode showed a reasonably good external electroluminescence (EL) quantum efficiency (0.7% at 100 A/m^2). However, a significant voltage drop across the device was noted due to the relatively high surface sheet resistance of the thin polymer film (∼1.8 kΩ/sq at 130 nm thickness) used as an anode and resulted in a reduced light output, especially at high operating voltages. Similar device performance using a highly conducting polymer as an electrode was reported for polymer light-emitting devices[19] and photovoltaic cells.[20]

More recently, we have shown that the surface sheet resistance of these polyalcohol-doped PEDOT:PSS films is largely dependent on the baking conditions, with the best sheet resistance achieved when the film is annealed close to the boiling point of the dopant.[21] The surface sheet resistance of the films varied from ∼600 to 1500 Ω/sq, depending upon the baking temperatures. Studies based on FT-IR and TGA clearly indicated the presence of free polyalcohol in the insufficiently baked films. The OLED device performance based on these conducting polymer anodes was greatly affected by the baking conditions of the conducting film anodes. Higher brightness, current density, and luminous power efficiency were observed from the devices using the anodes baked at temperatures close to the boiling point of dopant in comparison with those using the anodes baked at lower temperatures. The increased conductivity and uniformity of the properly baked conducting polymer anode device is responsible for the improvement in the device performance.

Silacyclopentadienes (siloles) are a new class of materials with good electron-transporting and/or fluorescent properties.[22−30] The silole ring has a low-lying lowest unoccupied molecular orbital (LUMO) level due to the $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the two exocyclic Si−C σ-bonds and the π^* orbital of the butadiene fragment, which results in a high electron affinity.[22,23] Efficient electron injection from Mg:Ag or CsF/Al cathodes to 2,5-bis-(2′,2′′-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PyPySPyPy) has been observed.[25,27,30] PyPySPyPy also exhibits nondispersive electron transport with a high mobility ($\sim 2.0 \times 10^{-4}$ cm^2/V s at an electric field $E = 0.64$ MV/cm) in either nitrogen or air.[24] High performance MOLED, with external electroluminescence (EL) quantum efficiencies up to ∼4.8% at 100 A/m^2, luminance over 10 000 cd/m^2, and low operating voltages (∼4.5 V at 100 cd/m^2), were demonstrated using siloles.[25−29] In this paper, we present low operating voltage and high luminance OLEDs using these siloles and conducting polymer anodes.

Experimental Section

OLEDs are fabricated using conducting polymers with various sheet resistances as anodes (without ITO) and Mg:Ag alloy or CsF/Al as a cathode. The chemical structures of the materials used in this study are shown in Figure 1.

The conducting polymer, poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT:PSS), was kindly provided by Agfa Gevaert N. V. Belgium as an aqueous dispersion (Orgacon PEDOT coating solution) or a precoated film on a poly(ethylene terephthalate) (PET) substrate (Orgacon specialty film). PEDOT:PSS supplied as precoated film on PET substrate by the manufacturer was used without any modification. The conducting polymer dispersion was spin-coated onto the cleaned glass substrate after filtration through a 0.45 μm polyvinyl difluoride (PVDF) filter. The polymer films were subsequently baked at 190 °C for 5 min on a hot plate under ambient conditions. This process was repeated as many times as necessary to obtain the desired sheet resistance (≤150 Ω/sq).

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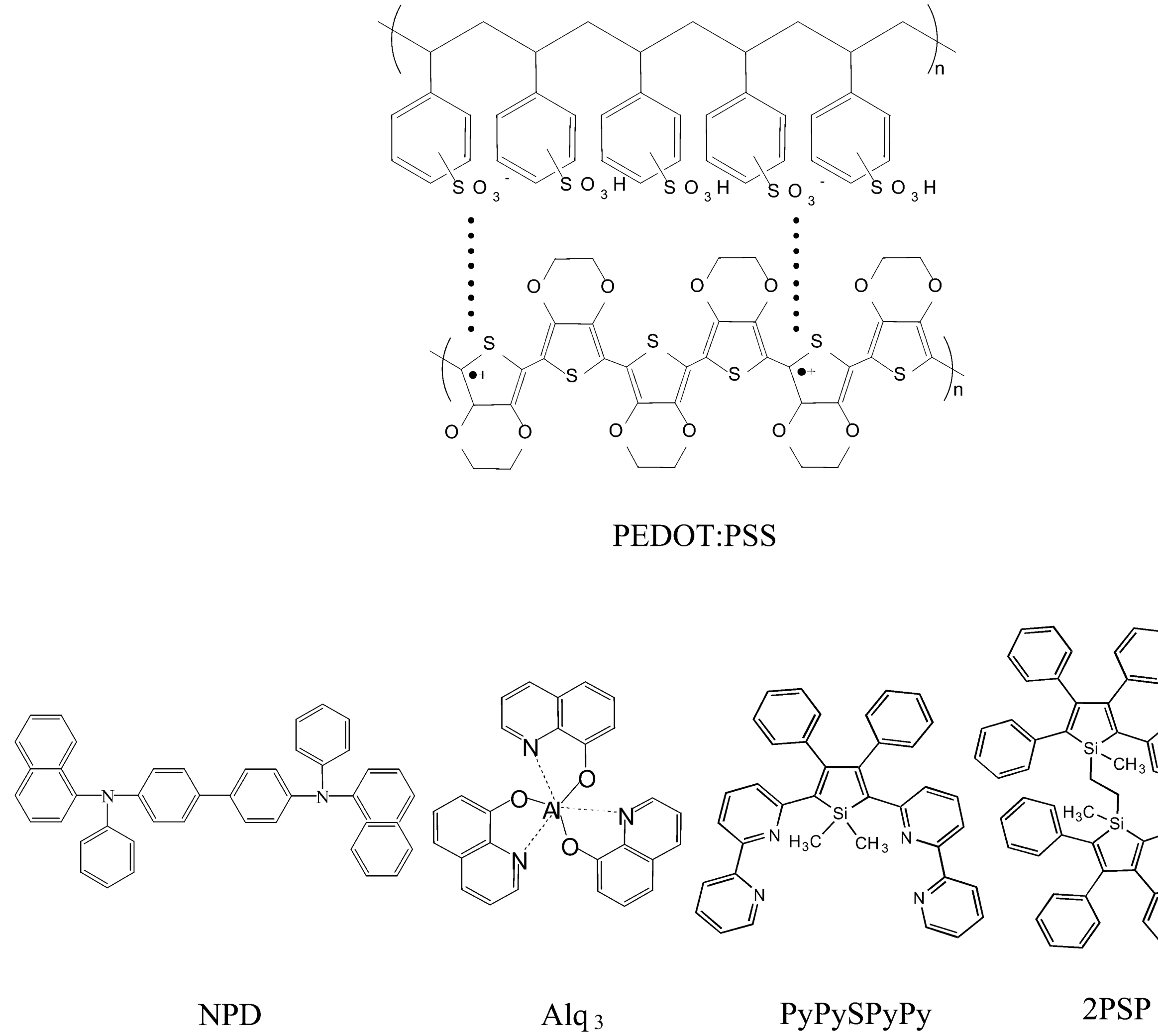

Figure 1. Chemical structures of the materials used in this study.

In some cases spin speed was adjusted to vary the thickness of the films. The thickness, in the range of 200−250 nm, was measured using a surface profilometer. The sheet resistance (R_s) was determined by four-point probe measurements. Assuming that the thickness of the films is uniform, the film resistivity (ρ) was calculated using the simple relationship: $\rho = R_s t$, where t is the film thickness. The hole transporter, *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (α-NPB), and the electron transporter/emitter, tris(8-hydroxyquinolinolato)-aluminum(III) (Alq_3), were purchased from H. W. Sands and TCI America, respectively. Alq_3 was purified by vacuum train sublimation and NPB was used without further purification. Two siloles, 2,5-bis-(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PyPySPyPy) and 1,2-bis(1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl)ethane (2PSP), were synthesized and purified by Chisso Corp.[22,23] Details of the device fabrication and characterization have been described elsewhere.[17,21] Multilayer light-emitting diodes were prepared in a vacuum chamber at a pressure of ~5 × 10^{-7} Torr. A 50 nm thick film of α-NPB was first deposited onto the patterned (2 mm line width) conducting polymer anode and used as a hole-transport layer (HTL). A detailed process of patterning the conducting polymers is described elsewhere.[31] Briefly, the polymer films are exposed to UV light (200−365 nm) through a photomask and the exposed part is removed by sonication in mild solvents such as alcohols and water. A 50−70 nm thick film of 2PSP or Alq_3 used as the emitting layer (EML) with an additional 10 nm thick film of PyPySPyPy used as the electron-transport layer (ETL) were sequentially deposited on top of the HTL. The total thickness of the organic layers is estimated to be ~110 nm on the basis of the deposition rate (typically 1−3 Å/s) of each material, measured by an in-situ quartz crystal microbalance with nanogram sensitivity. A 150-nm thick Mg:Ag film, prepared by coevaporation of Mg and Ag at a weight ratio of 10 to 1, was deposited onto the organic layers using a shadow mask and was used as the cathode material. Alternatively, a layer of CsF (0.7 nm) followed by Al (150 nm) was deposited and used as the cathode. Single layer “electron-only” devices were prepared on glass substrates in a vacuum chamber at a pressure of ~3 × 10^{-7} Torr, using two similar Mg:Ag or CsF/Al electrodes. Further details on the experimental procedure are described elsewhere.[30] Deposition rates of CsF, Mg, Ag, and Al were ~0.5, ~3−5, ~0.5, and ~1−2 Å/s, respectively. Current−voltage−luminance (*I*−*V*−*L*) measurements of the OLEDs were conducted using a Keithley 238 high current source measure unit and a Minolta LS-110 luminance meter. All the measurements were performed in a glovebox containing a dry, nitrogen atmosphere.

Results and Discussion

Optical transmittance of the conducting polymer films precoated on PET with various sheet resistances (Figure 2a) and prepared by multiple spin coating on glass with various thickness (Figure 2b) is shown and compared with that of conventional ITO on glass (30 Ω/sq).

The optical transmittance of the conducting polymer films is generally lower than that of ITO, regardless of the substrates. Much lower sheet resistance with rela-

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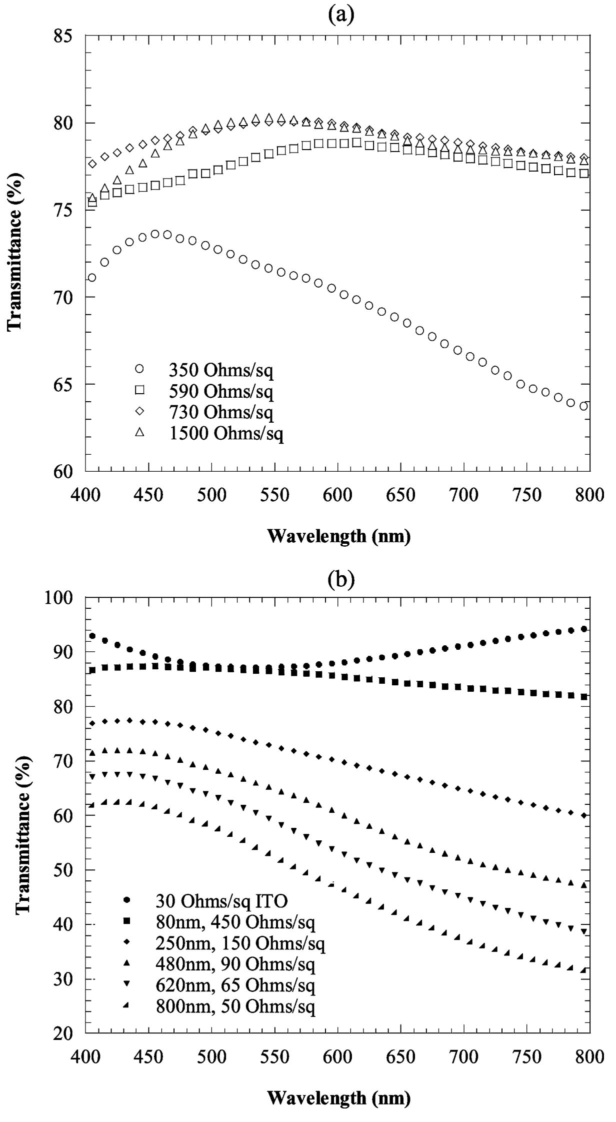

Figure 2. (a) The optical transmittance of the conducting polymer films with various sheet resistances precoated on plastic. (b) The optical transmittance of the conducting polymer films with various sheet resistances obtained by multiple coating on glass substrates as compared with that of conventional ITO on glass.

tively high transmittance was obtained from the films spin cast from the dispersion on a glass substrate. For example, a surface sheet resistance of 150 Ω/sq was measured from the spin cast films with 250 nm thickness. The average optical transmittance of this corresponding film in the visible region is higher than 70%, but it is still lower than that of ITO on glass (~90%). Glass (rather than PET) substrates were employed for the fabrication of the polymer films from the dispersions, since a relatively high baking temperature (much higher than the T_g of PET, ~85 °C) is necessary to achieve the lowest possible sheet resistance, as we reported earlier.[21]

A standard double-layer device using α-NPB as the hole-transporting material, Alq_3 as the electron transporter/light emitter, and a Mg:Ag cathode was fabricated using the patterned conducting polymers with various surface sheet resistance and compared with the one based on ITO anode. Figure 3 shows a plot of the current density (*J*)−voltage (*V*)−luminance (*L*) characteristics of the OLEDs.

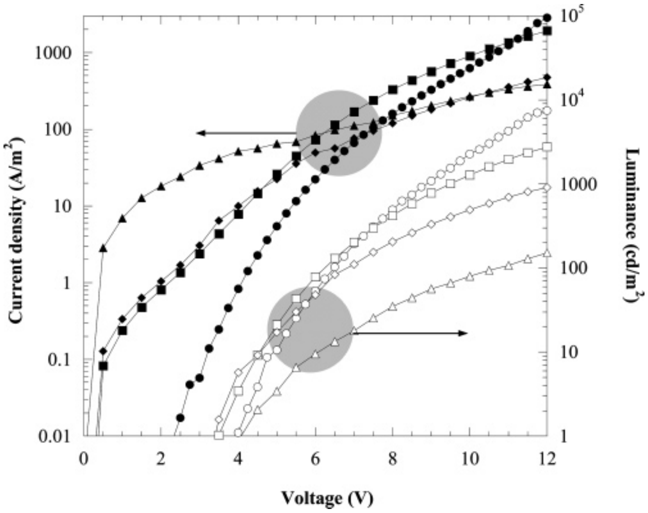

Figure 3. Plots of current density (*J*)−applied voltage (*V*)−luminance (*L*) of OLEDs using conducting polymers with various sheet resistance compared with ITO devices: circle, 30 Ω/sq ITO on glass; square, 150 Ω/sq PEDOT:PSS on glass; diamond, 590 Ω/sq PEDOT:PSS precoated on PET; triangle, 1500 Ω/sq PEDOT:PSS precoated on PET.

The changes in the *J*−V characteristics of the OLEDs directly reflect the electrical properties of the anodes used. It is clearly seen that the sheet resistance of the conducting polymer determines the device performance. The OLEDs using the PEDOT:PSS anodes with the highest sheet resistance (1500 Ω/sq) did not exhibit a diode behavior. In addition, most of the devices fabricated with the conducting polymer anodes showed higher leakage current at low operating voltage compared to the devices using ITO electrodes. This behavior is more severe for the devices fabricated with the conducting polymer films precoated on PET substrates and may be due to the poor contact between the conducting polymer and the organic hole-transporting layer. At high voltage, most of the devices suffer from limited current injection due to the high sheet resistance of the hole-injecting polymer electrode. A more interesting result is observed from the device fabricated onto the conducting polymer anode with the lowest sheet resistance of 150 Ω/sq. The device shows a comparable or even slightly better *J*−*V*−*L* characteristic compared to that using an ITO anode at low operating voltages. For instance, a current density of 100 A/m^2 was recorded at 6.25 and 7.5 V for devices using the conducting polymer and ITO anodes, respectively. A brightness of 100 cd/m^2 was achieved at ~6.25 and 6.5 V from the corresponding devices. However, the light output was greatly reduced at high voltage (>8 V), possibly due to the somewhat high sheet resistance, as predicted from the *J*−*V* characteristics that indicate limited current injection.

To further improve the device performance of the conducting polymer-based devices, we employed a bilayer CsF/Al cathode and compared the performance of the device with that using a Mg:Ag cathode. It is known that the introduction of ultrathin alkali metal halide layers between the organic film and the metal cathode leads to a significant enhancement in electron injection and the formation of quasi-Ohmic contacts.[32,33] Figure 4 shows the current density and luminance as a function of the applied voltage for OLEDs based on the following

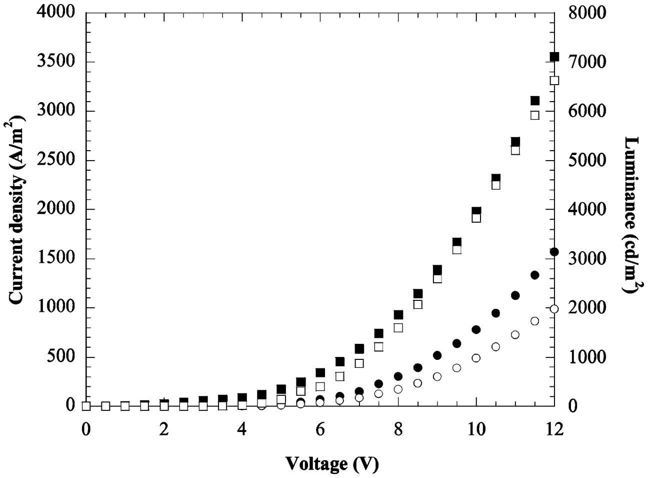

Figure 4. Plots of current density (J)−applied voltage (V)−luminance (L) of OLEDs using the following structures: PEDOT:PSS (150 Ω/sq) anode/NPD/Alq_3/Mg:Ag cathode [closed (J) and open (L) circles] or CsF/Al cathode [closed (J) and open (L) squares].

structures: PEDOT:PSS (150 Ω/sq) anode/NPD/Alq_3/Mg:Ag [closed (J) and open (L) circles] and PEDOT:PSS (150 Ω/sq) anode/NPD/Alq_3/CsF/Al [closed (J) and open (L) squares].

A comparison of the $J-V-L$ characteristics clearly indicates that the device performance is dramatically improved when a CsF/Al cathode is used. A consistently lower voltage was observed at the same current density for the device using CsF/Al as a cathode as compared to that using Mg:Ag. This improvement is attributed to a more efficient electron injection from the bilayer cathode. The device shows a very low operating voltage (4.5 and 7 V for 100 and 1000 cd/m^2, respectively) and high luminance (>8000 cd/m^2 at 12 V). This is the best device performance ever reported for OLEDs utilizing a conducting polymer as an anode without an ITO underlayer. Considering that the experimental conditions and device configuration have not been optimized, these results are quite promising. This improvement is presumably due to better electron injection from the CsF/Al cathode, which leads to better charge balance and efficient recombination of the holes and electrons in the light-emitting layer.

We have recently shown that the electron mobility of PyPySPyPy is 2 orders of magnitude higher than that of Alq_3.[24] Figure 5 shows a comparison of the external electroluminescence (EL) quantum efficiency for OLEDs based on Alq_3 as an emitter using PyPySPyPy and Alq_3 as electron transporters.

A dramatic increase in the external EL quantum efficiency as well as the luminance efficacy is observed from the device using PyPySPyPy as the electron transporter. An external EL quantum efficiency of 0.95% (0.6% without PyPySPyPy) and a luminance efficacy of 3.3 cd/A (1.9 cd/A without PyPySPyPy) was obtained from the OLEDs using PyPySPyPy as the electron transporter. This enhanced performance is due to the good balance of holes and electrons, since the electron mobility of PyPySPyPy is similar to the hole mobility of α-NPB.

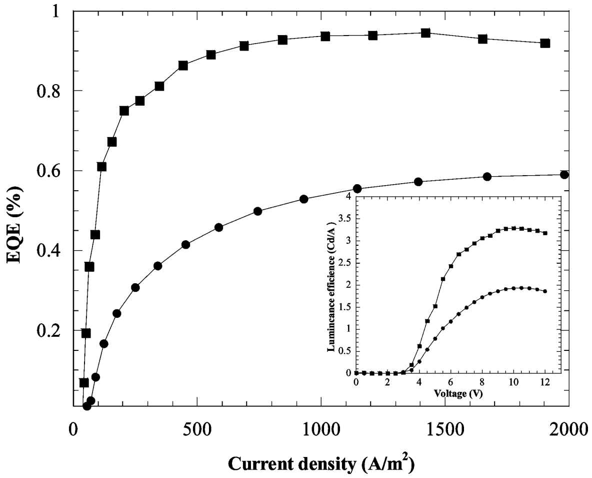

Figure 5. Plots of the external EL quantum efficiency vs current density of the OLEDs using Alq_3 as an emitter and PyPySPyPy as an electron transporter (square) compared with the one using Alq_3 as both emitter/electron transporter (circle). The inset shows the power efficiency of the corresponding devices.

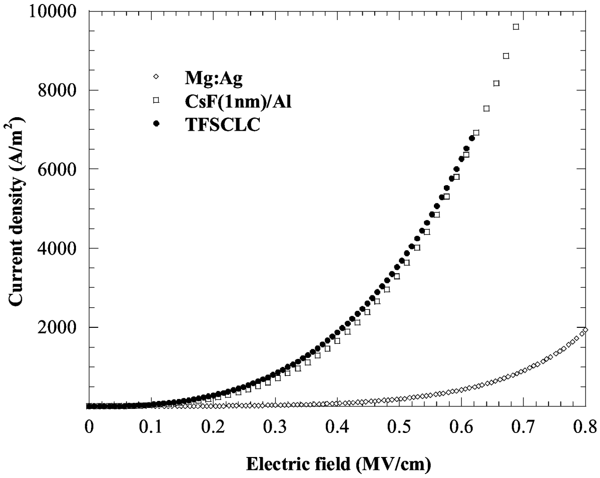

Figure 6. Current density vs electric field characteristics of devices based on Mg:Ag/PyPySPyPy/Mg:Ag (open diamonds) and CsF/Al/PyPySPyPy/CsF/Al (open squares) symmetric structures. The closed circles represent the TFSCL current calculated using the electron mobility obtained from the time of flight measurements.[24]

Electron-only devices were also fabricated to study the electron injection properties from different cathode materials to PyPySPyPy. Figure 6 shows the current density (J) vs electric field (E) characteristics of electron-only devices based on a ~250 nm thick PyPySPyPy single layer using either Mg:Ag alloy or a bilayer of CsF (1 nm)/Al as electrodes.

The data shown are for electron injection from the top Mg:Ag or CsF/Al electrode (cathode). Given the very large energy barrier for hole injection from the bottom Mg:Ag electrode (anode)[26] and the poor hole mobility of PyPySPyPy,[24] the measured $J-E$ characteristics reflect electron-only current conduction. The figure shows a very good agreement between the trap-free space charge limited current (TFSCLC) calculated using the modified Mott−Gurney equation[34] and the measured electron mobility of PyPySPyPy,[24] and the steady-state J−E

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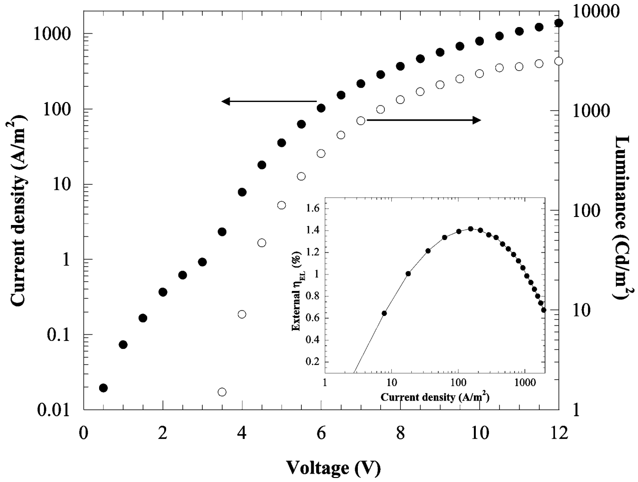

Figure 7. Current density (*J*)−applied voltage (*V*)−luminance (*L*) characteristics of the OLED based on the following structure: conducting polymer anode (150 Ω/sq)/NPD/2SPS/PyPySPyPy/CsF/Al device. The inset shows the plot of the external EL quantum efficiency at various current densities.

characteristics of the device using a CsF/Al cathode. On the other hand, a current density about 1−2 orders of magnitude lower than the TFSCLC is measured for the device using a Mg:Ag cathode, clearly showing injection-limited electron current. An injection efficiency of ~1 was estimated for the device using a CsF/Al contact, thus confirming the Ohmic character of this contact for electron injection into PyPySPyPy.[30] Employment of an electron transporter with a high electron mobility in combination with an unlimited injection of electrons from the Ohmic contact cathode is a good approach to lower the operating voltage when utilizing a high sheet resistance conducting polymer anode

In Figure 7 a plot of the current density and the luminance as a function of applied voltage for an OLED based on the structure PEDOT:PSS (150 Ω/sq) anode/NPD/2PSP/PyPySPyPy/CsF/Al cathode is shown. The inset shows the external EL quantum efficiency (η_{EL}) of the corresponding device as a function of current density.

Bright green emission ($\lambda = 500$ nm) at low voltage (3 V) and luminances of 100 and 1000 cd/m^2 were observed at 4.5 and 6.5 V, respectively. The device shows high external EL quantum efficiency (~1.42% at 100 A/m^2). However, the device appears to be still suffering from a voltage drop at the high operating voltage regime, due to the relatively higher surface resistance, which results in a decrease in luminance. A large deviation of the increase in luminance at high current density (>200 A/m^2) is caused by the high sheet resistance of the anode and results in a large drop in the external EL quantum efficiency. Considering the fact that only 70% of the emitted light is taken into account for the luminance, due to the relatively low transmittance of the conducting polymer anode, the overall device performance is significantly underestimated. It should be also noted that such a high device performance is obtained without doping the active organic layer or utilizing phosphorescent dyes.

We believe the relatively low sheet resistance of the polymer anode and the quasi-Ohmic contact between the cathode and the organic layer contribute to the low operating voltage and improvement in device performance. In addition, the high electron mobility of the PyPySPyPy electron transporter and the high PL quantum yield of the 2PSP emitter are also responsible for the enhancement of the overall device efficiency. However, it should be pointed out that the device performance is still much poorer and less stable than similar OLEDs fabricated on glass substrates and using ITO anodes. We have previously reported a high external EL quantum efficiency of 4.8% with very low operating voltage from the device fabricated on ITO using a similar structure.[25] The relatively high sheet resistance of the PEDOT:PSS anode, microshort and leakage current caused by the nonuniformity of the polymer electrode, and possible degradation due to the direct contact between the conducting polymer electrode and the organic layer upon high electric field may be all responsible for the inferior device performance. A study of the effect of the substrates and various buffer layers on the device performance is under way and will be published elsewhere.

Conclusion

We demonstrated high luminance OLEDs based on silole derivatives using a conducting polymer anode and a CsF/Al cathode. The low operating voltage (4.5 V for 100 cd/m^2 and 6.5 V for 1000 cd/m^2) is primarily attributable to the low sheet resistance of the conducting polymer anode, the Ohmic contact between the CsF/Al cathode and the electron-injecting PyPySPyPy layer, and the high electron mobility of PyPySPyPy. These results suggest that conducting polymers are promising candidates as anode materials and may eventually replace the most widely used ITO electrodes in many optoelectronic and electronic devices, especially those fabricated on flexible substrates.

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